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GENERALIZED EQUATIONS AND PROCEDURES
FOR THE CALCULATION OF DETONATION PARAMETERS

Case I.   Ideal Gaseous Mixtures

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AERONAUTICAL RESEARCH LABORATORY

MARCH 1956

WRIGHT AIR DEVELOPMENT CENTER

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ABSTRACT

The classical equations of detonation in gaseous mixtures are presented in generalized form involving only dimensionless quantities. This report sets forth a comprehensive procedure for the calculation of detonative Mach numbers and associated parameters for any combustible gaseous mixture.

The use of the method of calculation developed is illustrated by means of a sample calculation. For this purpose, calculations are presented for determination of detonation parameters for a stoichiometric mixture of hydrogen and oxygen at an initial temperature and pressure of 18°C and atmospheric pressure, respectively.

The calculation method developed is readily adaptable to computations by automatic computing machines as well as by manually-operated machines.

Graphs of basic data are presented for use in the sample calculations, and it is believed that these data will find practical use in other applications as well.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

ALDRO LINGARD
Colonel, USAF
Chief, Aeronautical Research
 Laboratory
Directorate of Research

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SYMBOL	DEFINITION	UNITS
a	Velocity of sound	cm/sec
a_1	Velocity of sound in the initial (unburned) mixture	cm/sec
a_2	Velocity of sound in the final (burned) mixture	cm/sec
B	Energy release function ($B = \dfrac{Jh}{a_1^2}$)	dimensionless
A, B, C, D, E,	Pertaining to components A, B, C, D, E, respectively, in the initial mixture	
c_{11}, c_{12}, c_{13},...	Miscellaneous constants	
C_p	Point or true molal heat capacity at constant pressure	cal/gm mole
C_{p_1}	Molal heat capacity at constant pressure for the initial mixture at the initial conditions (State 1)	cal/gm mole, °K
C_{p_2}	Molal heat capacity at constant pressure for the final mixture at the final conditions (State 2)	cal/gm mole, °K
$C_{p(U)}$, $C_{p(V)}$, $C_{p(W)}$, $C_{p(X)}$, $C_{p(Y)}$, $C_{p(Z)}$	Molal heat capacities of components U, V, W, X, Y, Z, respectively in the final mixture	cal/gm mole, °K
$\bar{C}_p$	Mean molal heat capacity	cal/gm mole, °K
$C_{p(i)}^{\bullet}$	Molal heat capacity at constant pressure for a component "i" in the initial mixture at the initial conditions (State 1)	cal/gm mole, °K
$C_{p(j)}$	Molal heat capacity at constant pressure for a component "j" in the final mixture at the final conditions (State 2)	cal/gm mole, °K
c_v	Specific heat at constant volume	cal/gm, °K

SYMBOL	DEFINITION	UNITS
c_{v_1}	Specific heat at constant volume for the initial mixture at the initial conditions (State 1)	cal/gm, °K
c_{v_2}	Specific heat at constant volume for the final mixture at the final conditions (State 2)	cal/gm, °K
C_v	Molal heat capacity at constant volume	cal/gm mole, °K
C_{v_1}	Molal heat capacity at constant volume for the initial mixture at the initial conditions	cal/gm mole, °K
C_{v_2}	Molal heat capacity at constant volume for the final mixture at the final conditions (State 2)	cal/gm mole, °K
$\bar{C}_v$	Mean molal heat capacity at constant volume	cal/gm mole, °K
$\bar{c}_{v_{1,0}}$	Mean specific heat at constant volume of initial mixture between State 1 (initial conditions) and State "0" (Reference State)	cal/gm, °K
$\bar{c}_{v_{2,0}}$	Mean specific heat at constant volume of final mixture between State 2 (final conditions) and State "0" (Reference State)	cal/gm, °K
D	Detonation velocity, i.e., velocity of the detonation wave with respect to the initial mixture	cm/sec
e	Specific internal energy	cal/gm
e°	Specific internal energy of a mixture at the reference state (State "0")	cal/gm
e_1	Specific internal energy of the initial mixture at the initial conditions (State 1)	cal/gm

SYMBOL	DEFINITION	UNITS
e_2	Specific internal energy of the final mixture at the final conditions (State 2)	cal/gm
F, G	Symbols representing elements contained in a chemical compound	
h	Energy release per unit mass of mixture	cal/gm
H	Enthalpy	cal/gm mole
H_i'	Enthalpy of compound "i" at the initial conditions (i.e., at t_1) relative to its standard state at temperature t_L	cal/gm mole
H_j'	Enthalpy of compound "j" at the initial conditions (i.e., at t_1) relative to it standard state at temperature t_L	cal/gm mole
ΔH_f	Heat of formation (The heat of formation of a compound represents the heat absorbed or evolved when one mole of the compound is formed from the elements in a reaction beginning and ending at some given temperature, with the reacting elements originally in the states of aggregation which are stable at that temperature).	cal/gm mole
$\Delta H_{f(i)}'$	Heat of formation of any component "i" in the initial mixture at the initial conditions (i.e., at temperature t_1)	cal/gm mole
$\Delta H_{f(j)}'$	Heat of formation of any component "j" in the final mixture at the initial conditions (i.e., at temperature t_1)	cal/gm mole
$\Delta H_{f(A)}'$, $\Delta H_{f(B)}'$, $\Delta H_{f(C)}'$, $\Delta H_{f(D)}'$, $\Delta H_{f(E)}'$	Heats of formation of components A, B, C, D, E, respectively, in the initial mixture at the initial conditions (i.e., at temperature t_1)	cal/gm mole

SYMBOL	DEFINITION	UNITS
$\Delta H'_{f(U)}$, $\Delta H'_{f(V)}$, $\Delta H'_{f(W)}$, $\Delta H'_{f(X)}$, $\Delta H'_{f(Y)}$, $\Delta H'_{f(Z)}$	Heats of formation of components U, V, W, X, Y, Z, respectively, in the final mixture <u>at the initial conditions</u> (i.e., at temperature t_1)	cal/gm mole
$\Delta H_{f_L}(j)$	Heat of formation of any component "j" in the final mixture at some temperature t_L, as found in the literature	cal/gm mole
$\Delta H_{f_L}(i)$	Heat of formation of any component "i" in the initial mixture at some temperature t_L, as found in the literature	cal/gm mole
ΔH_R	Heat of reaction, energy release per mole of initial mixture	cal/gm mole
$\sum H'_{e(i)}$	Sum of the enthalpies (at t_1) of the elements involved in the formation of one gram mole of compound "i", relative to the standard states of the elements at t_L	cal/gm mole of "i"
$\sum H'_{e(j)}$	Sum of the enthalpies (at t_1) of the elements involved in the formation of one gram mole of compound "j", relative to the standard states of the elements at t_L	cal/gm mole of "j"
J	Mechanical equivalent of heat; $J=4.185 \times 10^7$	dyne-cm/cal or ergs/cal
k_{11}, k_{12}, k_{13}, ...	Miscellaneous constants	
K_p	Equilibrium constant, in terms of partial pressures, for the dissociation of a compound (Units for this constant are atmospheres raised to a power which is dependent upon the particular dissociation reaction considered).	$(atmos)^{exp.}$
$K_{p(j)}$, $K'_{p(j)}$, $K''_{p(j)}$, ...	Equilibrium constants in terms of partial pressures for different dissociation reactions for any component "j" in the final mixture	$(atmos)^{exp.}$

SYMBOL	DEFINITION	UNITS
M	Mach number; $M = \dfrac{V}{a}$	dimensionless
M_1	Detonative Mach number, i.e., the Mach number of the detonation wave with respect to the initial mixture $(M_1 = \dfrac{V_1}{a_1})$	dimensionless
M_2	Mach number of the detonation wave with respect to the final mixture $(M_2 = \dfrac{V_2}{a_2})$	dimensionless
$\overline{M}_1$	Pseudo-Mach number, i.e., a very close approximation to the detonative Mach number, M_1; used for convenience only and defined by $\overline{M}_1^2 = M_1^2 + \dfrac{\left(\frac{r_4}{r}\right)^2}{M_1^2}$	dimensionless
$M_{w(A)},\ M_{w(B)},\ M_{w(C)},$ $M_{w(D)},\ M_{w(E)}$	Molecular weights of components A, B, C, D, E, respectively, in the initial mixture	gms/gm mole
M_{w_1}	Average molecular weight of the initial mixture	gms/gm mole
M_{w_2}	Average molecular weight of the final mixture	gms/gm mole
$M_{w(i)}$	Molecular weight of any component "i" in the initial mixture	gms/gm mole
$M_{w(j)}$	Molecular weight of any component "j" in the final mixture	gms/gm mole
$M_{w(U)},\ M_{w(V)},\ M_{w(W)},$ $M_{w(X)},\ M_{w(Y)},\ M_{w(Z)}$	Molecular weight of components U, V, W, X, Y, Z, respectively, in the final mixture	gms/gm mole
n	Number of moles	

SYMBOL	DEFINITION	UNITS
n_1	Total number of moles in initial mixture	
n_2	Total number of moles in final mixture	
n_i'	Number of moles of any component "i" in the initial mixture	
n_j	Number of moles of any component "j" in the final mixture	
$n_A', n_B', n_C', n_D', n_E'$	Number of moles of components A, B, C, D, E, respectively, in the initial mixture	
$n_U, n_V, n_W, n_X, n_Y, n_Z$	Number of moles of components U, V, W X, Y, Z, respectively, in the final mixture	
N	Number of atoms in one molecule of a given component of a mixture (always an integral value or zero)	
$^F N_i, ^G N_i, \ldots$	Number of atoms of element F, G..., respectively, in one molecule of any component "i" in the initial mixture (always an integral value or zero)	
$^F N_j, ^G N_j, \ldots$	Number of atoms of element F, G, ..., respectively, in one molecule of any component "j" in the final mixture (always an integral value or zero)	
p	Pressure	atmos
P_1	Total pressure for the initial mixture at the initial conditions (State 1)	atmos
P_2	Total pressure for the final mixture at the final conditions (State 2)	atmos

SYMBOL	DEFINITION	UNITS
p_i^i	Partial pressure of any component "i" in the initial mixture at the initial conditions (State 1)	atmos
p_j	Partial pressure of any component "j" in the final mixture at the final conditions (State 2)	atmos
$P_U, P_V, P_W, P_X, P_Y, P_Z$	Partial pressures of components U, V, W, X, Y, Z, respectively, in the final mixture at the final conditions (State 2)	atmos
P	Pressure (1.0133×10^6 dynes/cm^2 = 1 atmos)	dynes/cm^2
P_1	Total pressure of the initial mixture at the initial conditions (State 1)	dynes/cm^2
P_2	Total pressure of the final mixture at the final conditions (State 2)	dynes/cm^2
q	Heat added to the system	cal/gm
R	Universal gas constant; $R = 1.98719$	cal/gm mole, °K.
R_1	Specific gas constant for initial mixture at the initial conditions (State 1) $(R_1 = \dfrac{R}{M_{W_1}})$	cal/gm, °K
R_2	Specific gas constant for final mixture at the final conditions (State 2) $(R_2 = \dfrac{R}{M_{W_2}})$	cal/gm, °K
t	Temperature	°C
t_L	A reference temperature pertaining to data found in the literature	°C
t_1	Temperature at the initial conditions (State 1)	°C

LIST OF SYMBOLS (Cont'd)

SYMBOL	DEFINITION	UNITS
t_2	Temperature at the final conditions (State 2)	°C
T	Absolute temperature	°K
T_0	Datum or reference temperature	°K
T_1	Temperature at the initial conditions (State 1)	°K
T_2	Temperature at the final conditions (State 2)	°K
U, V, W, X, Y, Z	Pertaining to components U, V, W, X, Y, Z, respectively, in the final mixture	
v	Specific volume, i.e., volume per unit mass	cm^3/gm
V	Velocity	cm/sec
V_1	Velocity of detonation wave with respect to the initial mixture	cm/sec
V_2	Velocity of detonation wave with respect to the final mixture	cm/sec
w	Work done by the system	$\frac{ergs}{gm}$ or $\frac{(dyne-cm)}{gm}$
x	Mole fraction	
$x'_A, x'_B, x'_C, x'_D, x'_E$	Mole fractions of components A, B, C, D, E, respectively, in the initial mixture	
x'_i	Mole fraction of any component "i" in the initial mixture	
x_j	Mole fraction of any component "j" in the final mixture	

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SYMBOL	DEFINITION	UNITS
$x_U, x_V, x_W, x_X, x_Y, x_Z$	Mole fractions of components U, V, W, X, Y, Z, respectively, in the final mixture	
E	Dimensionless parameter (epsilon) used for convenience only and defined by $E = (\gamma_2^2 - 1)B$	dimensionless
Γ	Gamma Function, a dimensionless parameter used for convenience only and defined by $\Gamma = \dfrac{\gamma_1^2 - \gamma_1}{\gamma_1(\gamma_1 - 1)}$	dimensionless
θ	Symbol designating (or signifying) any parameter	
Δ	Symbol indicating difference	
γ	Point or true specific heat (or molal heat capacity) ratio for a mixture $\left(\gamma = \dfrac{C_p}{C_v}\right)$	dimensionless
γ_1	Specific heat (or molal heat capacity) ratio of the initial mixture at the initial conditions (State 1) $\left(\gamma_1 = C_{p_1}/C_{v_1}\right)$	dimensionless
γ_2	Specific heat (or molal heat capacity) ratio of the final mixture at the final conditions (State 2) $\left(\gamma_2 = C_{p_2}/C_{v_2}\right)$	dimensionless
ρ	Density, i. e., mass per unit volume	gm/cm^3
ρ_1	Density of initial mixture at the initial conditions (State 1)	gm/cm^3
ρ_2	Density of final mixture at the final conditions (State 2)	gm/cm^3

SYMBOLS	DEFINITION	UNITS
Σ	Symbol indicating summation	

Subscripts

1	Pertaining to the initial mixture at the initial conditions (State 1)	
2	Pertaining to the final mixture immediately behind the detonation wave at the final conditions (State 2)	
A, B, C, D, E	Pertaining to components A, B, C, D, E, respectively, in the initial mixture	
i	Pertaining to any component "i" in the initial mixture	
j	Pertaining to any component "j" in the final mixture	
L	Pertaining to data obtained from the literature	
o	Pertaining to a reference condition	
p	Pertaining to constant pressure	
v	Pertaining to constant volume	
U, V, W, X, Y, Z	Pertaining to components U, V, W, X, Y, Z, respectively, in the final mixture	

Left Superscripts

F, G, ...	Pertaining to elements F, G, ..., respectively	

Right Superscripts

"(°)" (Degree sign)	Pertaining to the standard state	

I. INTRODUCTION

The literature on the subject of detonation in gaseous mixtures dates back more than seventy years [16, 17, 18, 19, 20, 21, 22, 23, 24]. The majority of this literature has emphasized the prevention of detonation rather than its utilization. In connection with combustion in propulsive devices, the study of detonation prevention is important because of the destructive effects which may be associated with uncontrolled detonative combustion. On the other hand, useful application of detonative type combustion in propulsive devices appears to warrant consideration.

In the normal combustion processes occuring in the combustion chambers of present-day combustion devices, the flame speeds are on the order of 1 to 2 feet per second, whereas, rates of propagation for stable detonative type combustion are as high as 3000 to 12,000 feet per second for various gaseous mixtures.

In order to be able to reasonably evaluate the possible advantages of detonative type combustion in propulsion applications, it is necessary to be able to determine theoretically the values of all detonation parameters for various gaseous mixtures considered, under specified initial conditions. Determination of these detonation parameters can be accomplished experimentally; however, the necessary equipment is highly specialized and the techniques involved are not sufficiently developed as yet to permit the obtaining of values for these parameters readily under all desired initial conditions.

Methods of calculating detonation parameters utilizing directly the classical detonation equations have been reported by Zeldovich and Ratner [14] and Edse [15].

In performing calculations of detonation parameters for gaseous mixtures, it was found to be highly desirable to rearrange the classical (Chapman-Jouguet) detonation equations into generalized dimensionless form. In this report, the velocity of detonation is expressed in the form of the Mach number of the detonation wave relative to the unburned gases; the heat of reaction is expressed in the form of a dimensionless energy release function. The other detonation parameters are all expressed as dimensionless ratios of the quantities before and after the detonation wave, i.e., pressure ratio, temperature ratio, density ratio and molecular weight ratio. Several other dimensionless quantities are introduced to simplify further the graphical presentation of the generalized data and to facilitate calculations.

A method is presented in this report for the calculation of detonation velocities and other detonation parameters for gaseous mixtures. The use of the method of calculation developed is illustrated by means of a sample calculation. For this purpose, calculations are presented for determination of the detonation parameters for a stoichiometric mixture of hydrogen and oxygen at an initial temperature and pressure of 18°C and atmospheric pressure, respectively.

NOTE - This Technical Note was released by the author for publication in December 1954.

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A method is presented in this report for the calculation of detonation velocities and other detonation parameters for gaseous mixtures. The use of the method of calculation developed is illustrated by means of a sample calculation. For this purpose, calculations are presented for determination of the detonation parameters for a stoichiometric mixture of hydrogen and oxygen at an initial temperature and pressure of 18°C and atmospheric pressure, respectively.

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II. DERIVATION OF THE GENERALIZED EQUATIONS IN NON-DIMENSIONAL FORM

Some of the assumptions utilized in this section are introduced along with the presentation of particular equations. Other assumptions, more general in nature, will be noted before proceeding with the actual derivation of the equations.

It is assumed that the ideal gas law holds for the reactants and products at the initial and final conditions, respectively. This is equivalent to the assumption that the actual temperatures and pressures of the initial and final mixtures in all cases are in a region where the use of the ideal gas law results in negligible error. For the final mixture, this is a reasonable assumption in all cases in view of the extremely high temperatures occuring in detonation. For the initial mixture, this is a reasonable assumption if the initial conditions are sufficiently far from the critical conditions of pressure and temperature for each component so that compressibility is a negligible factor. Thus, in all cases where an equation of state has been required for describing the states of the initial and final mixtures at the initial and final conditions, respectively, the ideal gas law has been used.

The law of additives, which is valid for mixtures of ideal gases, is used to calculate the values of molecular weight (M_w) and molal heat capacity (C_p) for the initial and final mixtures.

It is assumed that chemical equilibrium is attained in the detonation wave.

The following equations of conservation across the detonation front are applicable:

Conservation of mass:

$$\rho_1 V_1 = \rho_2 V_2 \tag{1}$$

Conservation of momentum (considering only <u>normal</u> entry into the front):

$$P_1 + \rho_1 V_1^2 = P_2 + \rho_2 V_2^2 \tag{2}$$

Conservation of energy:

$$Je_1 + \frac{V_1^2}{2} + \frac{P_1}{\rho_1} + Jh = Je_2 + \frac{V_2^2}{2} + \frac{P_2}{\rho_2} \tag{3}$$

The velocity of sound in the initial and final mixtures, respectively, may be expressed in the form

$$a_1^2 = \gamma_1 \frac{P_1}{\rho_1} , \tag{4}$$

$$a_2^2 = \gamma_2 \frac{P_2}{\rho_2} . \tag{5}$$

The assumption is made here that the adiabatic law holds for infinitesimal changes in the initial mixture at the initial conditions and in the final mixture at the final conditions. This is merely the usual assumption made in deriving the expression for the speed of sound.

Since $M_1 = V_1/a_1$ and $M_2 = V_2/a_2$, then with equations (4) and (5),

$$V_1^2 = M_1^2 a_1^2 = \frac{\gamma_1 M_1^2 P_1}{\rho_1} \,, \tag{6}$$

$$V_2^2 = M_2^2 a_2^2 = \frac{\gamma_2 M_2^2 P_2}{\rho_2} \,. \tag{7}$$

By definition, the energy release function is

$$B = \frac{Jh}{a_1^2} \,. \tag{8}$$

From equations (8) and (4),

$$Jh = Ba_1^2 = \frac{B \gamma_1 P_1}{\rho_1} \,. \tag{9}$$

From the conservation of momentum, equation (2) and equations (6) and (7), the pressure ratio across the detonation front may be expressed as

$$\frac{P_2}{P_1} = \frac{\gamma_1 M_1^2 + 1}{\gamma_2 M_2^2 + 1} \,. \tag{10}$$

From the conservation of mass equation (1) and equations (6) and (7),

$$\frac{\rho_2}{\rho_1} = \left(\frac{M_1^2}{M_2^2}\right) \left(\frac{\gamma_1}{\gamma_2}\right) \left(\frac{P_1}{P_2}\right) \,, \tag{11}$$

and from equations (10) and (11), the density ratio may be expressed in the form

$$\frac{\rho_2}{\rho_1} = \left(\frac{\gamma_1 M_1^2}{\gamma_1 M_1^2 + 1}\right) \left(\frac{\gamma_2 M_2^2 + 1}{\gamma_2 M_2^2}\right) \,. \tag{12}$$

From equations (12) and (10),

$$\frac{P_2}{P_1} \frac{\rho_1}{\rho_2} = \frac{\gamma_2 M_2^2}{(\gamma_2 M_2^2 + 1)^2} \cdot \frac{(\gamma_1 M_1^2 + 1)^2}{\gamma_1 M_1^2} \cdot \qquad (13)$$

The equation of state for ideal gases may be expressed in the following form:

$$\frac{P}{\rho} = \frac{JRT}{M_w} , \qquad (14)$$

Applying equation (14) to the state conditions before and after the detonation wave, designated by subscripts 1 and 2, respectively, the following relationship is obtained:

$$\frac{P_2}{P_1} \frac{\rho_1}{\rho_2} = \frac{T_2 M_{w_1}}{T_1 M_{w_2}} . \qquad (15)$$

The dimensionless quantity $\dfrac{T_2 M_{w_1}}{T_1 M_{w_2}}$ is referred to hereafter as "the temperature-molecular weight ratio." From equations (13) and (15), the following expression for the temperature-molecular weight ratio is obtained:

$$\frac{T_2}{T_1} \frac{M_{w_1}}{M_{w_2}} = \frac{\gamma_2 M_2^2}{(\gamma_2 M_2^2 + 1)^2} \cdot \frac{(\gamma_1 M_1^2 + 1)^2}{\gamma_1 M_1^2} \cdot \qquad (16)$$

The mass and momentum conservation equations ((1) and (2)) have been utilized to obtain non-dimensional expressions for $\dfrac{P_2}{P_1}, \dfrac{\rho_2}{\rho_1}$ and $\dfrac{T_2 M_{w_1}}{T_1 M_{w_2}}$ (equations (10), (12) and (16)).

In order to similarly transform the conservation of energy equation (3), consideration of the internal energy term is required.

The first law of thermodynamics can be expressed as

$$dq = de + \frac{1}{J} dw . \qquad (17)$$

For the case where the only force acting on the system is a fluid pressure, $dw = Pdv$, and equation (17) becomes

$$dq = de + \frac{1}{J} Pdv . \qquad (18)$$

Differentiating equation (18) with respect to T, holding v constant, gives the following relationship:

$$\left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial e}{\partial T}\right)_v . \tag{19}$$

By definition, the specific heat at constant volume is

$$c_v = \left(\frac{\partial q}{\partial T}\right)_v , \tag{20}$$

and it follows from equation (19) that

$$c_v = \left(\frac{\partial e}{\partial T}\right)_v . \tag{21}$$

For ideal gases, c_v is independent of pressure (or volume) and therefore is a function of temperature only. Hence, the following expression may be obtained from equation (21):

$$c_v = \frac{de}{dT}, \tag{22}$$

or

$$de = c_v dT, \tag{23}$$

or

$$\Delta e = \int c_v dT. \tag{24}$$

For the internal energy per unit mass before and after passage through the detonation wave, respectively, equation (24) becomes

$$e_1 - (e_o)_{\text{initial mixture}} = \int_{T_o}^{T_1} (c_v)_{\text{initial mixture}} \, dT, \tag{25}$$

$$e_2 - (e_o)_{\text{final mixture}} = \int_{T_o}^{T_2} (c_v)_{\text{final mixture}} \, dT, \tag{26}$$

where subscripts 1 and 2 refer to the conditions before and after the detonation wave, respectively, and subscript "o" refers to the reference temperature T_o. Now, introducing $\bar{c}_v$ as a mathematical convenience, equations (25) and (26) become

$$e_1 - (e_0)_{\text{initial mixture}} = \bar{c}_{v_{1,o}}(T_1 - T_0), \tag{27}$$

$$e_2 - (e_0)_{\text{final mixture}} = \bar{c}_{v_{2,o}}(T_2 - T_0), \tag{28}$$

where

$\bar{c}_{v_{1,o}}$ = the mean specific heat at constant volume for the initial mixture between state 1 and the reference state (T_0),

$\bar{c}_{v_{2,o}}$ = the mean specific heat at constant volume for the final mixture between state 2 and the reference state (T_0).

The reference temperature T_0 will be taken to be absolute zero. In order to facilitate simplification of the generalized detonation equations, two assumptions will be made which the authors do not feel will appreciably affect the accuracy of the final generalized equations. It is assumed that the internal energy of the initial mixture at the reference temperature $(T_0 = 0°\text{K})$ is equal to the internal energy of the final mixture at the reference temperature $(T_0 = 0°\text{K})$, i.e.,

$$(e_0)_{\text{initial mixture}} = (e_0)_{\text{final mixture}}.$$

The mean specific heats, $\bar{c}_{v_{1,o}}$ and $\bar{c}_{v_{2,o}}$, will be replaced by the point properties c_{v_1} and c_{v_2}, respectively. This latter substitution or assumption will permit expression of the generalized detonation equations in terms only of the point properties of the initial and final mixtures, respectively.

Based on the foregoing statements, equations (27) and (28) may be combined to yield the following expression for the difference in internal energies across the detonation wave:

$$e_2 - e_1 = c_{v_2}T_2 - c_{v_1}T_1 . \tag{29}$$

Utilizing equation (29), the conservation of energy equation (3) becomes

$$Jc_{v_1}T_1 + \frac{P_1}{\rho_1} + \frac{V_1^2}{2} + Jh = Jc_{v_2}T_2 + \frac{P_2}{\rho_2} + \frac{V_2^2}{2} . \tag{30}$$

For the case of ideal gases, from equation (14),

$$T_1 = \frac{M_{w_1}}{JR} \cdot \frac{P_1}{\rho_1} \quad \text{and} \quad T_2 = \frac{M_{w_2}}{JR} \cdot \frac{P_2}{\rho_2} . \tag{31}$$

Using equations (31), the energy equation (30) may be written

$$\left(-\frac{c_{v_1}M_{w_1}}{R}+1\right)\frac{P_1}{\rho_1}+\frac{V_1^2}{2}+Jh=\left(-\frac{c_{v_2}M_{w_2}}{R}+1\right)\frac{P_2}{\rho_2}+\frac{V_2^2}{2}\ . \tag{32}$$

Since $c_{v_1}M_{w_1}=C_{v_1}$, and $c_{v_2}M_{w_2}=C_{v_2}$, and since, for ideal gases,

$R=C_{p_1}-C_{v_1}=C_{p_2}-C_{v_2}$, equation (32) becomes

$$\left(\frac{C_{p_1}}{C_{p_1}-C_{v_1}}\right)\frac{P_1}{\rho_1}+\frac{V_1^2}{2}+Jh=\left(\frac{C_{p_2}}{C_{p_2}-C_{v_2}}\right)\frac{P_2}{\rho_2}+\frac{V_2^2}{2}\ , \tag{33}$$

and, since $\gamma_1=C_{p_1}/C_{v_1}$, and $\gamma_2=C_{p_2}/C_{v_2}$, the following equation is obtained from equation (33):

$$\frac{\gamma_1}{\gamma_1-1}\ \frac{P_1}{\rho_1}+\frac{V_1^2}{2}+Jh=\frac{\gamma_2}{\gamma_2-1}\ \frac{P_2}{\rho_2}+\frac{V_2^2}{2}\ . \tag{34}$$

Equation (34) is the approximate energy equation utilized by D. G. Samaras in his paper on endothermic and exothermic discontinuities (1948)[11] and involves approximations believed to be negligible, as discussed above.

From equations (6), (7), (9) and (34), the following equation is obtained:

$$\frac{\gamma_1}{\gamma_1-1}+\frac{\gamma_1 M_1^2}{2}+\gamma_1 B=\left(\frac{\gamma_2}{\gamma_2-1}+\frac{\gamma_2 M_2^2}{2}\right)\frac{P_2}{P_1}\frac{\rho_1}{\rho_2}\ , \tag{35}$$

and, from equations (35) and (13),

$$B=\left(\frac{\gamma_2}{\gamma_2-1}+\frac{\gamma_2 M_2^2}{2}\right)\cdot\frac{\gamma_2 M_2^2}{\left(\gamma_2 M_2^2+1\right)^2}\cdot\frac{\left(\gamma_1 M_1^2+1\right)^2}{\gamma_1^2 M_1^2}-\frac{1}{\gamma_1-1}-\frac{M_1^2}{2}\ . \tag{36}$$

This is a form of the Hugoniot equation, in non-dimensional form, based on the energy equation (34).

The Chapman-Jouguet hypothesis that the product gases (final mixture) leave the detonation front at a velocity equal to the local speed of sound in those gases may be expressed in the form

$$M_2=1.0\ . \tag{37}$$

With this substitution, equation (36) reduces to

$$B = \left(\frac{\gamma_2}{\gamma_2 - 1} + \frac{\gamma_2}{2}\right) \cdot \frac{\gamma_2}{(\gamma_2 + 1)^2} \cdot \frac{(\gamma_1 M_1^2 + 1)^2}{\gamma_1^2 M_1^2} - \frac{1}{\gamma_1 - 1} - \frac{M_1^2}{2} \quad , \tag{38}$$

which, upon rearrangement, gives the following simplified expression:

$$B = \frac{1}{\gamma_2^2 - 1}\left[\frac{M_1^2}{2} + \left(\frac{\gamma_2}{\gamma_1}\right)^2\left(\frac{1}{2 M_1^2} + \gamma_1\right)\right] - \frac{1}{\gamma_1 - 1} \quad . \tag{39}$$

This is a non-dimensional form of the equation commonly referred to as the Chapman-Jouguet equation, based on the energy equation (34).

Applying the Chapman-Jouguet hypothesis (equation (37)) to equations (10), (12) and (16)), expressions for the pressure ratio, density ratio and temperature-molecular weight ratio across the detonation wave, in non-dimensional form, may be obtained as follows:

$$\frac{P_2}{P_1} = \frac{1}{\gamma_2 + 1}(\gamma_1 M_1^2 + 1) \quad , \tag{40}$$

$$\frac{\rho_2}{\rho_1} = \frac{\gamma_2 + 1}{\gamma_2}\left(\frac{\gamma_1 M_1^2}{\gamma_1 M_1^2 + 1}\right) \quad , \tag{41}$$

$$\frac{T_2 \, M_{W_1}}{T_1 \, M_{W_2}} = \frac{\gamma_2}{(\gamma_2 + 1)^2} \cdot \frac{(\gamma_1 M_1^2 + 1)^2}{\gamma_1 M_1^2} \quad . \tag{42}$$

The above three equations, together with equation (39), are the non-dimensional generalized detonation equations which form the basis for calculations and graphical presentations in this report.

Equations (40), (41) and (42) are presented graphically in Figures 6, 7 and 8, respectively. In each of these three graphs, $\gamma_1 M_1^2$ has been made the abscissa. Figure 9 is a plot of M_1^2 vs $\gamma_1 M_1^2$ with lines of constant γ_1 and is presented merely to show the overall range of the term $\gamma_1 M_1^2$ encountered in the detonation of gaseous mixtures.

The interrelationship between the variables P_2/P_1, ρ_2/ρ_1 and $\frac{T_2 M_{W_1}}{T_1 M_{W_2}}$ (the dependent variables shown in equations (40), (41) and (42), respectively) is presented in

graphical form in Figure 10. It will be noted that this graph is simply a plot of equation (15), which is the equation of state for ideal gases.

III. REARRANGEMENT OF THE CHAPMAN-JOUGUET EQUATION

The Chapman-Jouguet equation, (39), may be rearranged and expressed in the following manner in order to facilitate the graphical presentation and to simplify the computational procedure:

$$M_1^2 + \left(\frac{\gamma_2}{\gamma_1}\right)^2 \frac{1}{M_1^2} = 2\left(\gamma_2^2 - 1\right) B + 2 \frac{\gamma_2^2 - \gamma_1}{\gamma_1\left(\gamma_1 - 1\right)} . \tag{43}$$

Equation (43) may be simplified by replacing the terms on the left hand side of the equation by a single symbol, $\overline{M}_1^2$, and replacing the two terms on the right hand side of the equation by simple functions of the dimensionless parameters E and Γ, respectively. The term $\overline{M}$, is introduced at this point and is given the name "pseudo-Mach number." The parameter E is hereafter referred to as "the dimensionless parameter epsilon," and the dimensionless parameter Γ is hereafter referred to as "the gamma function." Thus, equation (43) may be expressed in either of the following two forms:

$$\overline{M}_1^2 = 2\left(\gamma_2^2 - 1\right) B + 2 \frac{\gamma_2^2 - \gamma_1}{\gamma_1\left(\gamma_1 - 1\right)} , \tag{44}$$

or

$$\overline{M}_1^2 = 2E + 2\Gamma , \tag{45}$$

where

$$\overline{M}_1^2 = M_1^2 + \left(\frac{\gamma_2}{\gamma_1}\right)^2 \frac{1}{M_1^2} , \tag{46}$$

$$E = \left(\gamma_2^2 - 1\right) B , \tag{47}$$

$$\Gamma = \frac{\gamma_2^2 - \gamma_1}{\gamma_1 (\gamma_1 - 1)} \cdot \qquad (48)$$

It should be noted that equations (43), (44) and (45) are merely rearrangements of the non-dimensional form of the Chapman-Jouguet equation, based on the energy equation (34).

Equations (47), (48), (45) and (46) are presented graphically in Figures 1, 2, 3 and 4 respectively. These figures present the non-dimensional Chapman-Jouguet equation in graphical form. Figure 5 is a plot of γ_2/γ_1 vs γ_2 with lines of constant γ_1 and is presented merely to show the overall range of γ_2/γ_1 encountered in the detonation of gaseous mixtures.

IV. BASIC DATA REQUIRED

A. Data on heats of formation for the reactants at the initial temperature and pressure, or these data at a standard temperature and pressure in conjunction with data on the change C_p with temperature between the standard conditions and the initial conditions.

B. Data on molal heat capacity, $C_{p(i)}$, for each component of the initial mixture at the initial conditions.

C. Data on molal heat capacity, $C_{p(j)}$, for each component of the final mixture at the final conditions in the detonation wave.

D. Data on equilibrium constants for dissociation reactions involving the components of the final mixture at the final conditions in the detonation wave.

V. DISCUSSION OF THE CALCULATION PROCEDURE

The calculation procedure based on the generalized detonation equations derived in this report is presented in detail in Appendix I. Immediately preceding this procedure a complete outline of the steps involved is given in order to facilitate its use.

Indications are that previous methods for calculating detonation parameters have utilized directly the classical Chapman-Jouguet equations involving dimensional quantities, 6, 12, 13, 14, 15/ whereas in this report the calculation procedure utilizes generalized equations and non-dimensional parameters throughout.

This method of calculation involves a process of successive approximations or a trial-and-error procedure. This is necessitated by the fact that a direct solution of the generalized equations is still impractical, if not impossible. The fact that dissociation of the product gases is taken into account in the calculations results in a triple trial-and-error procedure. This procedure involves the assignment of arbitrary values to final pressure, temperature and composition and then, by a method of successive approximations, the values of these quantities are adjusted so that the calculated values approach the assumed values. Dimensionless quantities and graphical presentation of the generalized data, as described above, are used to simplify and streamline considerably the calculation procedure. The method presented provides for a rapid convergence of the trial-and-error calculations by simple graphical techniques. The calculation procedure also provides for continual self-checking of results at intermediate points throughout the entire calculation, i.e., errors can be detected and discarded with little loss of time.

Considerable effort has been expended in the preparation of this method to insure that the information contained therein is clearly understandable to any research scientist who might have occasion to be working in this field (aeronautical, mechanical, chemical, electrical or propulsion engineer, or chemist). The calculation procedure, charts and graphs are presented so that even those not experienced in the detonation field can readily utilize the information presented to obtain accurate values of the required detonation parameters by routine manual calculation with a minimum of time, ingenuity, instruction and/or supervision. Where extensive data at different initial conditions and for various gaseous mixtures are desired, this method is also very readily adaptable to calculations by automatic computing machines.

VI. DISCUSSION OF THE SAMPLE CALCULATION

A sample calculation utilizing the calculation procedure presented in this report is given in Appendix III. Calculations are presented for the determination of the detonation parameters for a stoichiometric mixture of hydrogen and oxygen at an initial temperature and pressure of 18°C and atmospheric pressure, respectively.

Results obtained in these calculations (taking into consideration atomic oxygen in the reaction products and utilizing consistent data throughout for specific heats and equilibrium constants in the range of the final temperature) indicated a detonation temperature and pressure of 3536°K and 17.2 atmospheres, respectively, and a detonation velocity of 8962 ft/sec. Results obtained by this calculation procedure neglecting the dissociation of molecular oxygen but still utilizing the same consistent data for specific heat and equilibrium constants gave values of the detonation temperature and pressure of 3593°K and 17.3 atmospheres, respectively, and a detonation velocity of 8991 ft/sec.*

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*This calculation was performed by the authors, but detailed calculations are not presented in this report.

Calculated data obtained from literature sources indicate a detonation temperature and pressure of 3583°K and 18.05 atmospheres, respectively, and a detonation velocity of 9203 ft/sec, these values having been calculated neglecting the dissociation of molecular oxygen[12,13]. The difference between the calculated data presented in this report and that reported in the literature is probably due to (a) the use of slightly different specific heat and equilibrium constant data in calculating the detonation parameters, and (b) the simplifying assumptions utilized in deriving the generalized equations, which apparently did not affect greatly the accuracy of the final results.

Preliminary experimental data obtained by the authors in a one-inch diameter detonation tube showed very close agreement (approximately 1-1/2%) with the data calculated by the procedure reported. The experimental value obtained for the detonation velocity was 9100 ft/sec.

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APPENDIX I

CALCULATION PROCEDURE

Detailed Outline of Calculation Steps
Detailed Calculation Procedure

For convenience in using this calculation procedure, a detailed outline of the steps involved is presented below.

Step 1. Proposed Scheme of Reaction

Step 2. Setting-Up of the Partial Pressure Equations for Use in the Calculation of the Composition of the Final Mixture

Step 3. Solution of the Simultaneous Partial Pressure (p_j) Equations in General Terms

Step 4. Fixing of the Initial Composition, n_i'

Step 5. Particular Solution of the Partial Pressure (p_j) Equations for a Specific Initial Mixture Composition (n_i')

Step 6. Fixing of the Initial Pressure, p_1

Step 7. Fixing of the Initial Temperature, t_1

Step 8. Calculation of the Properties of the Initial Mixture

Step 9. Assumption of the Final Pressure, p_2

Step 10. Assumption of the Final Temperature, T_2

Step 11. Determination of Numerical Values of the Equilibrium Constants for the Dissociation Reactions

Step 12. Calculation of the Partial Pressures $(p_j's)$ in the Final Mixture

Step 13. Determination of the Total Number of Moles (n_2) of the Final Mixture.

Step 14. Calculation of the Composition $(n_j's)$ of the Final Mixture

Step 15. Calculation of the Properties of the Final Mixture

Step 16. Calculation of the Heat of Reaction, ΔH_R

Step 17. Calculation of the Energy Release Function, B

Step 18. Determination of the Value of the Gamma Ratio, γ_2 / γ_1

Step 19. Calculation of the Molecular Weight Ratio, M_{w_2} / M_{w_1}

Step 20. Determination of the Value of the Dimensionless Parameter E

Step 21. Determination of the Value of the Gamma Function, Γ

Step 22. Determination of the Value of the Pseudo-Mach Number (Squared), $\overline{M}_1^2$

Step 23. Determination of the Value of the Detonative Mach Number (Squared), M_1^2

Step 24. Determination of the Value of $\gamma_1 M_1^2$

Step 25. Determination of the Value of the Temperature-Molecular Weight Ratio, $T_2 M_{w_1} / T_1 M_{w_2}$

Step 26. Calculation of the Final Temperature, T_2

Step 27. Determination of the Value of the Pressure Ratio, p_2/p_1

Step 28. Calculation of the Final Pressure, p_2

Step 29. Calculation of the Detonative Mach Number, M_1

Step 30. Calculation of the Detonation Velocity, D

Step 31. Calculation of Additional Data
  a. Density ratio, ρ_2/ρ_1
     (or Volume Ratio, v_1/v_2)

  b. Initial Density, ρ_1 (or $\frac{1}{v_1}$)

  c. Final Density, ρ_2 (or $\frac{1}{v_2}$)

The detailed calculation procedure is presented below and follows the outline given directly above.

Step 1. Proposed Scheme of Reaction

Set down initially a proposed scheme of reaction, including all possible or probable products:

$$n'_A A + n'_B B + \ldots \longrightarrow n_U U + n_V V + \ldots, \qquad (49)$$

n'_A and n'_B being known quantities, n_U and n_V being initially unknown quantities. The number of possible products included in this reaction scheme will depend upon experience and information available on the particular reaction being investigated.

The calculation procedure should be started on the basis of the above proposed reaction scheme. After the first calculation of composition, based on the first assumed temperature and pressure, it may be apparent that one or more of the products in the proposed reaction scheme is

present only in negligible amount. If this is the case, then it may be advisable to modify the above proposed scheme of reaction to eliminate the negligible constituents before proceeding with the second calculation of composition.

Step 2.   Setting-Up of the Partial Pressure (p_j) Equations for use in the Calcula-. tion of the Composition of the Final mixture

a. Dissociation Reactions and Equilibrium Equations

Set down dissociation reactions involving each of the products included in the above reaction scheme, along with the corresponding equilibrium equations expressed <u>in terms of the partial pressures</u> <u>of the constituents</u>. For example, if H_2O, H_2 and O_2 are three of the components of the final mixture, then

$$H_2O \rightleftharpoons H_2 + 1/2\ O_2 \tag{50}$$

and

$$\frac{p_{O_2}^{\frac{1}{2}}\ p_{H_2}}{p_{H_2O}} = K_{p\ (H_2O)} = \text{equilibrium constant.} \tag{51}$$

In selecting the dissociation reactions to be used in these calculations, care must be excercised to insure that the equilibrium equations obtained are independent equations. Each successive dissociation reaction written must involve a new component of the final mixture if the corresponding equilibrium equation is to be independent of the other equilibrium equations. Another factor to be considered in the selection of the dissociation reactions to be used is the availability of equilibrium constant data for particular reactions.

b. Additional Equations Required

The dissociation reactions have provided a number of independent equations involving the partial pressure of each component of the final mixture. In order to solve for each of these partial pressures, the total number of independent equations available must equal the number of components in the final mixture. Independent equations required in addition to the equilibrium equations are obtained from (1) application of Dalton's Law, i.e., summation of partial pressures, and (2) application of the law of conservation of mass for each element involved in the proposed scheme of reaction.

c. Summation of Partial Pressures in the Final Mixture

Set down the equation for the summation of the partial pressures of the components of the final mixture:

$$p_U + p_V + p_W + \ldots = \sum_j p_j = p_2 . \tag{52}$$

d. Conservation of Mass for Each Element

Set down the mass-balance equation stating the conservation of atomic type for each chemical element involved in the proposed reaction scheme. The number of these mass-balance equations is equal to the number of chemical elements involved. The law of conservation of mass yields, for elements F and G, the following two equations:

For element F:

$$n'_A {}^F N_A + n'_B {}^F N_B + \ldots = n_U {}^F N_U + n_V {}^F N_V + \ldots , \tag{53}$$

or

$$\sum_i n'_i {}^F N_i = \sum_j n_j {}^F N_j . \tag{54}$$

For element G:

$$n'_A {}^G N_A + n'_B {}^G N_B + \ldots = n_U {}^G N_U + n_V {}^G N_V + \ldots , \tag{55}$$

or

$$\sum_i n'_i {}^G N_i = \sum_j n_j {}^G N_j . \tag{56}$$

Divide each mass balance equation by n_2 (value initially unknown) as shown below. For element F, the equation obtained is

$$\frac{1}{n_2} \sum_i n'_i {}^F N_i = \sum_j \frac{n_j}{n_2} {}^F N_j ; \tag{57}$$

and, similarly, for element G,

$$\frac{1}{n_2} \sum_i n'_i {}^G N_i = \sum_j \frac{n_j}{n_2} {}^G N_j . \tag{58}$$

Substitute into the mass balance equation for each element the following equality, obtained from Dalton's Law of Additive Pressures and the ideal-gas law:

$$\frac{n_j}{n_2} = \frac{p_j}{p_2} \ . \tag{59}$$

This yields a mass balance equation, for each element, in terms of the partial pressures (p_j's) of components of the final mixture. For element F, this yields the equation

$$\frac{1}{n_2} \sum_i n'_i \, {}^F N_i = \sum_j \frac{p_j}{p_2} \, {}^F N_j \ , \tag{60}$$

and, for element G, the equation

$$\frac{1}{n_2} \sum_i n'_i \, {}^G N_i = \sum_j \frac{p_j}{p_2} \, {}^G N_j \ ; \tag{61}$$

or, rearranging slightly, for element F,

$$\frac{1}{n_2} \sum_i n'_i \, {}^F N_i = \frac{1}{p_2} \sum_j p_j \, {}^F N_j \ , \tag{62}$$

and, for element G,

$$\frac{1}{n_2} \sum_i n'_i \, {}^G N_i = \frac{1}{p_2} \sum_j p_j \, {}^G N_j \ . \tag{63}$$

As stated above, the number of these mass balance equations (equations (62) and (63)) is equal to the number of chemical elements involved in the proposed reaction scheme. Any two of the mass balance equations may be combined to yield an independent equation in terms of the partial pressures (p_j's), by elimination of n_2 and p_2. For example, for elements F and G, dividing equation (62) by (63) yields

$$\frac{\sum\limits_i n'_i \, {}^F N_i}{\sum\limits_i n'_i \, {}^G N_i} = \frac{\sum\limits_j p_j \, {}^F N_j}{\sum\limits_j p_j \, {}^G N_j} \ . \tag{64}$$

If there are <u>three</u> chemical elements involved in the reaction scheme, an additional independent equation in terms of the partial pressures (p_j's) may be obtained by using a <u>new combination</u> of mass balance equations. If <u>more than three</u> elements are involved, additional independent equations in terms of the partial pressures may be obtained in the same manner.

Step 3. Solution of the Simultaneous Partial Pressure (p_j) Equations in General Terms

Step 2 has provided a number of independent partial pressure equations equal to the number of components in the final mixture. Solve these equations simultaneously to obtain a general solution. When the number of products of reaction is small, this solution of the simultaneous equations may be accomplished by direct algebraic methods. When the number of reaction products is large, it may be desirable to utilize methods of solution such as those reported by Edse,[8] Huff and Calvert,[5] Huff and Morrell,[9] Hershfelder,[10] etc.

Particular solutions for specific initial mixtures (n'_i) are obtained from the general solution by fixing the initial mixture composition (Steps 4 and 5).

Step 4. Fixing of the Initial Mixture Composition, n'_i

Fix the initial mixture composition, n'_i, at the value to be used throughout the remainder of the calculations.

Step 5. Particular Solution of the Partial Pressure (p_j) Equations for a Specific Initial Mixture Composition (n'_i)

Substitute the numerical value for the initial mixture composition (n'_i), assigned in Step 4, into the general solution obtained in Step 3, to obtain a particular solution of the partial pressure (p_j) equations for a specific initial mixture composition.

Step 6. Fixing of the Initial Pressure, P_1

Fix the initial pressure, P_1, at the value to be used throughout the remainder of the calculations.

Step 7. Fixing of the Initial Temperature, t_1

Fix the initial temperature, t_1, at the value to be used throughout the remainder of the calculations.

Step 8. Calculation of the Properties of the Initial Mixture

a. Mole Fraction, x'_i

$$x'_A = \frac{n'_A}{n'_A + n'_B + \ldots} \, , \qquad (65)$$

or

$$x'_i = \frac{n'_i}{\sum_i n'_i} = \frac{n'_i}{n_1} \, . \qquad (66)$$

b. Molecular Weight, M_{w_1}

$$M_{w_1} = x'_A M_{w(A)} + x'_B M_{w(B)} + \ldots \qquad (67)$$

$$= \sum_i x'_i M_{w(i)} \, .$$

c. Molal Heat Capacity at Constant Pressure, C_{p_1}

$$C_{p_1} = x'_A C'_{p(A)} + x'_B C'_{p(B)} + \ldots \qquad (68)$$

$$= \sum_i x'_i C'_{p(i)} \, .$$

d. Specific Heat Ratio (or Molal Heat Capacity Ratio), γ_1

$$\gamma_1 = \frac{C_{p_1}}{C_{v_1}} = \frac{C_{p_1}}{C_{p_1} - R} \, . \qquad (69)$$

e. Heat of Formation*, $\Delta H'_{f(i)}$

Calculate the heat of formation of each component of the initial mixture at the initial conditions.

$$\Delta H'_{f(i)} = \Delta H_{f_L(i)} - H'_i + \sum H'_{e(i)} \, . \qquad (70)$$

If the component "i" is an element in its standard state of aggregation at t_1, then, by definition, it is apparent that its heat of formation $\Delta H'_{f(i)}$ is equal to zero, e.g., $\Delta H'_{f(H_2)}$ and $\Delta H'_{f(O_2)}$ are equal to zero when t_1 is in a region where hydrogen and

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* In this report, the heat of formation is taken to be positive when heat is evolved. If enthalpy data for this calculation cannot be found in the literature, it can be calculated readily from available C_p data.

oxygen are normally diatomic gases.

Step 9. Assumption of the Final Pressure, p_2

Assume a value for the final pressure, p_2.

Step 10. Assumption of the Final Temperature, T_2

Assume a value for the final temperature, T_2.

Step 11. Determination of the Numerical Values of the Equilibrium Constants for the Dissociation Reactions

Obtain the numerical values of the equilibrium constant for each of the dissociation reactions considered in Step 2, at the assumed temperature (T_2), either from available data in the literature or by calculation.

Because of the trial-and-error nature of the overall calculation procedure, it is advisable to make a plot of equilibrium constant versus temperature for each of the dissociation reactions in the temperature range in which T_2 is expected to be. It is necessary that this be done at the very beginning of the calculation procedure in order to insure that consistent data are used and thereby facilitate rapid convergence of the trial-and-error calculations.

Step 12. Calculation of the Partial Pressures (p_j's) in the Final Mixture

Using the equation(s) obtained in Step 5 in conjunction with the equilibrium equations set forth in Step 2, par. a, determine the numerical value of the partial pressure (p_j) of each constituent of the final mixture.

Step 13. Determination of the Total Number of Moles (n_2) of the Final Mixture

Set down the overall mass balance equation for the proposed scheme of reaction:

$$n'_A M_{w(A)} + n'_B M_{w(B)} + \ldots = n_U M_{w(U)} + n_V M_{w(V)} + \ldots , \qquad (71)$$

or

$$\sum_i n'_i M_{w(i)} = \sum_j n_j M_{w(j)} . \qquad (72)$$

Substitute in equation (72) the relationship

$$n_j = \frac{p_j}{p_2} n_2 , \qquad (73)$$

obtained from equation (59); then

$$\sum_i n'_i M_{w(i)} = \frac{n_2}{P_2} \sum_j P_j M_{w(j)} , \tag{74}$$

and

$$n_2 = P_2 \frac{\sum_i n'_i M_{w(i)}}{\sum_j P_j M_{w(j)}} . \tag{75}$$

This gives the total number of moles of final mixture corresponding to the number of moles of initial mixture shown in the proposed scheme of reaction (i.e., $n'_A + n'_B + \ldots$).

Step 14. Calculation of the Composition (n_j's)

Again using the relationship

$$n_j = \frac{P_j}{P_2} n_2 , \tag{73}$$

obtained from equation (59), calculate the number of moles (n_j) of each component in the final mixture.

Step 15. Calculation of the Properties of the Final Mixture

a. Mole Fraction, x_j

$$x_U = \frac{n_U}{n_2} = \frac{P_U}{P_2} , \tag{76}$$

or

$$x_j = \frac{n_j}{n_2} = \frac{P_j}{P_2} . \tag{77}$$

b. Molecular Weight, M_{w_2}

$$M_{w_2} = x_U M_{w(U)} + x_V M_{w(V)} + \ldots = \sum_j x_j M_{w(j)} . \tag{78}$$

c. Molal Heat Capacity at Constant Pressure, C_{p_2}

Determine the value of C_{p_2} at the above assumed value of T_2 (Step 10), using values of $C_{p(j)}$ obtained from the literature.

$$C_{p_2} = x_U C_{p(U)} + x_V C_{p(V)} + \ldots = \sum_j x_j C_{p(j)} . \tag{79}$$

d. Specific Heat Ratio (or Molal Heat Capacity Ratio), γ_2

$$\gamma_2 = \frac{C_{p2}}{C_{v_2}} = \frac{C_{p2}}{C_{p_2} - R} . \tag{80}$$

If C_p data cannot be found in the literature, it can be readily calculated from available enthalpy data.

e. Heat of Formation*, $\Delta H'_{f(j)}$

Calculate the heat of formation of each component of the final mixture at the initial conditions.

$$\Delta H'_{f(j)} = \Delta H_{f_L}(j) - H'_j + \sum H'_{e(j)} . \tag{81}$$

Step 16. Calculation of the Heat of Reaction, Energy Release per Mole of Initial Mixture (ΔH_R)

$$\Delta H_R = \frac{n_U \Delta H'_{f(U)} + n_V \Delta H'_{f(V)} + \ldots - n'_A \Delta H'_{f(A)} - n'_B \Delta H'_{f(B)} - \ldots}{n_A + n_B + \ldots}, \tag{82}$$

or

$$\Delta H_R = \frac{\sum_j n_j \Delta H'_{f(j)} - \sum_i n'_i \Delta H'_{f(i)}}{n_1} . \tag{83}$$

Step 17. Calculation of the Energy Release Function, B

By equations (8), (4) and (31) and by definition of "h" and ΔH_R,

_____

* See footnote in Step 8, par. e.

$$B = \frac{Jh}{a_1^2} = \frac{M_{w_1}h}{\gamma_1 RT_1} \cdot \frac{\Delta H_R}{\gamma_1 RT_1} . \tag{84}$$

Step 18. Determination of the Value of the Gamma Ratio, $\dfrac{\gamma_2}{\gamma_1}$

Calculate this ratio from values of γ_1 and γ_2 or obtain from Figure 5.

Step 19. Calculation of the Molecular Weight Ratio, $\dfrac{M_{w_2}}{M_{w_1}}$

Calculate this ratio from values of M_{w_1} and M_{w_2}.

Step 20. Determination of the Value of the Dimensionless Parameter E

Calculate E from values of γ_2 and B or obtain from Figure 1.

$$E = \left(\gamma_2^2 - 1 \right) B \tag{47}$$

Step 21. Determination of the Value of the Gamma Function, Γ

Calculate Γ from values of γ_1 and γ_2 or obtain from Figure 2.

$$\Gamma = \frac{\gamma_2^2 - \gamma_1}{\gamma_1 \left(\gamma_1 - 1 \right)} \tag{48}$$

Step 22. Determination of the Value of Pseudo-Mach Number (Squared), $\overline{M}_1^2$

Calculate $\overline{M}_1^2$ from values of E and Γ or obtain from Figure 3.

$$\overline{M}_1^2 = 2E + 2\Gamma , \tag{45}$$

or

$$\overline{M}_1^2 = 2 \left(\gamma_2^2 - 1 \right) B + 2 \frac{\gamma_2^2 - \gamma_1}{\gamma_1 \left(\gamma_1 - 1 \right)} . \tag{44}$$

Step 23. Determination of the Value of the Detonative Mach Number (Squared), M_1^2

Obtain the value of M_1^2 from Figure 4.

$$\overline{M}_1^2 = M_1^2 + \frac{\left(\gamma_2 / \gamma_1 \right)^2}{M_1^2} . \tag{46}$$

Step 24. Determination of the Value of $\gamma_1 M_1^2$

Calculate the value of $\gamma_1 M_1^2$ from values of γ_1 and M_1^2 or obtain from Figure 9.

Step 25. Determination of the value of the Temperature-Molecular Weight Ratio, $\dfrac{T_2 M_{w_1}}{T_1 M_{w_2}}$

Calculate the value of $\dfrac{T_2 M_{w_1}}{T_1 M_{w_2}}$ from values of $\gamma_1 M_1^2$ and γ_2 or obtain from Figure 8. From equation (42),

$$\frac{T_2}{T_1}\frac{M_{w_1}}{M_{w_2}} = \frac{\gamma_2}{(\gamma_2+1)^2}\left(\gamma_1 M_1^2 + \frac{1}{\gamma_1 M_1^2} + 2\right). \tag{85}$$

Step 26. Calculation of the Final Temperature, T_2

Calculate the value of T_2 from values of $\dfrac{T_2 M_{w_1}}{T_1 M_{w_2}}$, $\dfrac{M_{w_2}}{M_{w_1}}$ and T_1.

$$T_2 = \frac{T_2 M_{w_1}}{T_1 M_{w_2}} \cdot \frac{M_{w_2}}{M_{w_1}} \cdot T_1. \tag{86}$$

If this calculated value of T_2 does not check the assumed T_2 (Step 10), re-assume T_2 and repeat Steps 10 through 26. In order to facilitate rapid convergence between calculated and assumed values, the following procedure may be used. After two calculations of T_2, plot calculated T_2 versus assumed T_2 and draw a line through these two points, intersecting the 45° line. The value of T_2 at the point of intersection usually is a very good indication of the correct value of T_2 corresponding to the assumed p_2. This value of T_2 should be used as the assumed T_2 for third trial. A typical plot is shown in Figure 11.

Step 27. Determination of the Value of the Pressure Ratio, $\dfrac{p_2}{p_1}$

Calculate the value of $\dfrac{p_2}{p_1}$ using the values of γ_2 and $\gamma_1 M_1^2$ corresponding to the final checked value of T_2 obtained in the trial-and-error calculations of Steps 10 through 26, or obtain from Figure 6. From equation (40), since $\dfrac{P_2}{P_1}$ is numerically equal to $\dfrac{p_2}{p_1}$,

$$\frac{P_2}{P_1} = \frac{1}{\gamma_2 + 1} (\gamma_1 M_1^2 + 1) . \tag{87}$$

Step 28. Calculation of the Final Pressure, p_2

$$p_2 = \frac{P_2}{P_1} \cdot P_1 . \tag{88}$$

If this calculated value of p_2 does not check the assumed p_2 (Step 9), re-assume p_2 and repeat Steps 9 through 28 until the calculated and assumed values agree.

The graphical procedure outlined under Step 26 may be used to facilitate rapid convergence between calculated and assumed values of p_2.

Step 29. Calculation of the Detonative Mach Number, M_1

Calculate M_1 from the value of M_1^2 (Step 23) corresponding to the final checked values of p_2 and T_2 (Steps 26 through 28).

Step 30. Calculation of the Detonation Velocity, D

Since $D = V_1 = M_1 a_1$, then with equations (4) and (14),

$$D = M_1 \sqrt{\frac{J \gamma_1 R T_1}{M_{w_1}}} . \tag{89}$$

Step 31. Calculation of Additional Data

a. Density Ratio, $\frac{\rho_2}{\rho_1}$ (or Volume Ratio, $\frac{v_1}{v_2}$)

Calculate $\frac{\rho_2}{\rho_1}$ (or $\frac{v_1}{v_2}$) from the final checked values of $\frac{P_2}{P_1}$

and $\frac{T_2 M_{w_1}}{T_1 M_{w_2}}$ obtained in the trial-and-error calculations of Steps 26

through 28, or obtain from Figure 10.

$$\frac{\rho_2}{\rho_1} = \frac{P_2}{P_1} \Big/ \frac{T_2 M_{w_1}}{T_1 M_{w_2}} . \tag{15}$$

b. Initial Density, ρ_1 (or $\frac{1}{v_1}$)

By equation (14), for the initial mixture,

$$\rho_1 = \frac{M_{w_1} P_1}{JRT_1} .$$ (90)

c. Final Density, ρ_2 (or $\frac{1}{v_2}$)

$$\rho_2 = \frac{\rho_2}{\rho_1} \cdot \rho_1 .$$ (91)

APPENDIX II

GRAPHS OF BASIC DATA--
EQUILIBRIUM CONSTANTS AND
MOLAL HEAT CAPACITIES

As pointed out in the Calculation Procedure in this report, it is desirable that consistent data on equilibrium constants and molal heat capacities be available. Since the sample calculation presented in this report (Appendix III) is for a stoichiometric hydrogen-oxygen system, the necessary equilibrium constant data and molal heat capacity data for this system are presented in this appendix.

Values of the equilibrium constants (K_p's) as a function of the absolute temperature for H_2O, H_2 and O_2 are presented graphically in Figures 12 through 15, respectively.

Values of the molal heat capacities (C_p's) as a function of absolute temperature for H_2O, H_2, O_2 and OH are presented graphically in Figures 16 through 19, respectively.

The range of temperature in all these figures extends from 2000° to 5000°K, and it is expected that this range will cover all cases to be encountered in the detonation of gaseous mixtures.

In each of the figures described above, a smooth curve was drawn through the data plotted in order to insure that consistent data would be available for the trial-and-error calculations.

It is believed that these graphs of basic data described above will find practical use in other applications, particularly in other combustion calculations where trial-and-procedures are involved and where consistent thermodynamic data are essential.

APPENDIX III

SAMPLE CALCULATION

CALCULATION OF DETONATIVE MACH NUMBER AND ASSOCIATED PARAMETERS FOR H_2 - O_2 MIXTURES

The step numbers used below are the same as those given in the calculation procedure outlined in Appendix I.

Step 1.   Proposed Scheme of Reaction

$$n'_A A + n'_B B \longrightarrow n_U U + n_V V + n_W W + n_X X + n_Y Y + n_Z Z \tag{92}$$

or, specifically. for H_2 - O_2 mixtures,

$$n'_{H_2} H_2 + n'_{O_2} O_2 \longrightarrow N_{H_2O} H_2O + n_{H_2} H_2 + n_{O_2} O_2 + n_{OH} OH + n_H H + n_O O \ . \tag{93}$$
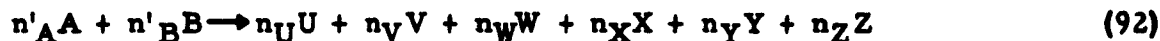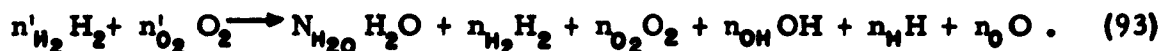
Step 2.   Setting-Up of the Partial Pressure (p_j) Equations

a. Dissociation Reactions

(1) $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$ $\tag{94}$

$$K_{p_{(H_2O)}} = \frac{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}}{p_{H_2O}} \ . \tag{95}$$

(2) $H_2O \rightleftharpoons \frac{1}{2}H_2 + OH$ $\tag{96}$

$$K'_{p_{(H_2O)}} = \frac{p_{H_2}^{\frac{1}{2}} \cdot p_{OH}}{p_{H_2O}} \ . \tag{97}$$

(3) $\frac{1}{2}H_2 \rightleftharpoons H$ $\tag{98}$

$$K_{p_{(H_2)}} = \frac{p_H}{p_{H_2}^{\frac{1}{2}}} \ . \tag{99}$$

(4) $\frac{1}{2}O_2 \rightleftharpoons O$ $\tag{100}$

$$K_{p_{(O_2)}} = \frac{p_O}{p_{O_2}^{\frac{1}{2}}} \ . \tag{101}$$

b. Summation of the Partial Pressures in the Final Mixture

$$p_U + p_V + p_W + p_X + p_Y + p_Z = \sum_j p_j = p_2 \ , \tag{102}$$

or, specifically, for H_2 - O_2 mixtures,

$$p_{H_2O} + p_{H_2} + p_{O_2} + p_{OH} + p_H + p_O = p_z \, . \tag{103}$$

c. Conservation of Mass for Each Element

Using equation (64),

$$\frac{\sum_i n_i' \, {}^F N_i}{\sum_i n_i' \, {}^G N_i} = \frac{\sum_j p_j \, {}^F N_j}{\sum_j p_j \, {}^G N_j} \, , \tag{64}$$

and taking elements F and G to be O_2 and H_2, respectively, then

$$\frac{n_{O_2}'}{n_{H_2}'} = \frac{p_{H_2O} + 2 p_{O_2} + p_{OH} + p_O}{2 p_{H_2O} + 2 p_{H_2} + p_{OH} + p_H} \, , \tag{104}$$

or

$$\left(2 \frac{n_{O_2}'}{n_{H_2}'} - 1\right) p_{H_2O} + 2 \frac{n_{O_2}'}{n_{H_2}'} p_{H_2} + \frac{n_{O_2}'}{n_{H_2}'} p_H + \left(\frac{n_{O_2}'}{n_{H_2}'} - 1\right) p_{OH} - 2 p_{O_2} - p_O = 0. \tag{105}$$

Step 3. Solution of the Simultaneous Partial Pressure (p_j) Equations in General Terms

Step 2 has provided the following six independent partial pressure equations, which are sufficient to determine the partial pressures of each of the six components in the final mixture.

$$K p_{(H_2O)} = \frac{p_{H_2} \, p_{O_2}^{\frac{1}{2}}}{p_{H_2O}} \, , \tag{95}$$

$$K' p_{(H_2O)} = \frac{p_{H_2}^{\frac{1}{2}} \, p_{OH}}{p_{H_2O}} \, , \tag{97}$$

$$K p_{(H_2)} = \frac{p_H}{p_{H_2}^{\frac{1}{2}}} \, , \tag{99}$$

$$Kp_{(O_2)} = \frac{p_0}{p_{O_2}^{\frac{1}{2}}} , \tag{101}$$

$$p_{H_2O} + p_{H_2} + p_{O_2} + p_{OH} + p_H + p_O = p_2 , \tag{103}$$

$$\left(2\frac{n'_{O_2}}{n'_{H_2}} - 1\right) p_{H_2O} + 2\frac{n'_{O_2}}{n'_{H_2}} p_{H_2} + \frac{n'_{O_2}}{n'_{H_2}} p_H + \left(\frac{n'_{O_2}}{n'_{H_2}} - 1\right) p_{OH} - 2p_{O_2} - p_O = 0 . \tag{105}$$

Rearranging equations (95), (97), (99) and (101),

$$p_{O_2} = \left(\frac{Kp_{(H_2O)} \ p_{H_2O}}{p_{H_2}}\right)^2 , \tag{106}$$

$$p_{OH} = \frac{Kp_{(H_2O)} \ p_{H_2O}}{p_{H_2}^{\frac{1}{2}}} , \tag{107}$$

$$p_H = Kp_{(H_2)} \ p_{H_2}^{\frac{1}{2}} , \tag{108}$$

$$p_O = Kp_{(O_2)} \ p_{O_2}^{\frac{1}{2}} = \frac{Kp_{(O_2)} \ Kp_{(H_2O)} \ p_{H_2O}}{p_{H_2}} , \tag{109}$$

and substituting these relationships into equations (103) and (105), respectively, the following two independent quadratic equations in terms of two variables, p_{H_2O} and p_{H_2}, are obtained:

$$\left(\frac{Kp_{(H_2O)}}{p_{H_2}}\right)^2 p_{H_2O}^2 + \left(\frac{K'p_{(H_2O)}}{p_{H_2}^{\frac{1}{2}}} + \frac{Kp_{(O_2)} \ Kp_{(H_2O)}}{p_{H_2}} + 1\right) p_{H_2O} + \left(p_{H_2} + Kp_{(H_2)} p_{H_2}^{\frac{1}{2}} - p_2\right) = 0, \tag{110}$$

$$2\left(\frac{Kp_{(H_2O)}}{p_{H_2}}\right)^2 p_{H_2O}^2 + \left[\frac{Kp_{(O_2)} \ Kp_{(H_2O)}}{p_{H_2}} - \left(\frac{n'_{O_2}}{n'_{H_2}} - 1\right)\frac{K'p_{(H_2O)}}{p_{H_2}^{\frac{1}{2}}} - 2\frac{n'_{O_2}}{n'_{H_2}} + 1\right] p_{H_2O}$$
$$- \frac{n'_{O_2}}{n'_{H_2}}\left(2 p_{H_2} + Kp_{(H_2)} p_{H_2}^{\frac{1}{2}}\right) = 0 . \tag{111}$$

Step 4. Initial Composition

For the purpose of this sample calculation, a stoichiometric mixture of hydrogen and oxygen will be considered, the initial composition being given by

$$n'_{H_2} H_2 + n'_{O_2} O_2 , \tag{112}$$

where

$$n'_{H_2} = 1 \quad \text{and} \quad n'_{O_2} = \frac{1}{2} ,$$

or

$$H_2 + \frac{1}{2} O_2 .$$
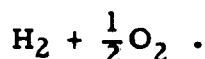
Step 5. Particular Solution of the Partial Pressure (p_j) Equations

From the values for initial composition given in Step 4,

$$\frac{n'_{O_2}}{n'_{H_2}} = \frac{1}{2} . \tag{113}$$

Substitution of the numerical value of this ratio into the general partial pressure equations (Equations (110) and (111)) obtained in Step 3 yields the following particular solution for a stoichiometric mixture of hydrogen and oxygen:

$$\left(\frac{K_{p_{(H_2O)}}}{p_{H_2}} \right)^2 p_{H_2O}^2 + \left(\frac{K_{p_{(O_2)}} K_{p_{(H_2O)}}}{p_{H_2}} + \frac{K'_{p_{(H_2O)}}}{p_{H_2}^{\frac{1}{2}}} + 1 \right) p_{H_2O}$$

$$+ \left(p_{H_2} + K_{p_{(H_2)}} p_{H_2}^{\frac{1}{2}} - p_2 \right) = 0 \tag{114}$$

and

$$2 \left(\frac{K_{p_{(H_2O)}}}{p_{H_2}} \right)^2 p_{H_2O}^2 + \left[\frac{K_{p_{(O_2)}} K_{p_{(H_2O)}}}{p_{H_2}} + \frac{K'_{p_{(H_2O)}}}{2 p_{H_2}^{\frac{1}{2}}} \right] p_{H_2O}$$

$$- \left(p_{H_2} + \frac{1}{2} K_{p_{(H_2)}} p_{H_2}^{\frac{1}{2}} \right) = 0 . \tag{115}$$

Step 6. Initial Pressure

For the purpose of this sample calculation, the initial pressure is fixed at 1 atmos., i.e.,

$$P_1 = 1 \text{ atmos.}$$

and

$$P_1 = 1.0133 \times 10^6 \text{ dynes/cm}^2.$$

Step 7. Initial temperature

For the purpose of this sample calculation, the initial temperature is fixed at 18°C, i.e.,

$$t_1 = 18°C.$$

and

$$T_1 = 291°K.$$

Step 8. Properties of the Initial Mixture

a. Mole Fractions

$$X'_{H_2} = \frac{n'_{H_2}}{n'_{H_2} + n'_{O_2}} = \frac{1}{1 + \frac{1}{2}} = \frac{2}{3} \; ;$$

$$X'_{O_2} = \frac{n'_{O_2}}{n'_{H_2} + n'_{O_2}} = \frac{\frac{1}{2}}{1 + \frac{1}{2}} = \frac{1}{3} \; ;$$

$$\sum_i X_i = X'_{H_2} + X'_{O_2} = 1.$$

b. Molecular Weight

$$M_{W_1} = X'_{H_2} \; M_{W(H_2)} + X'_{O_2} \; M_{W(O_2)}$$

$$= (\frac{2}{3}) (2.0160) + (\frac{1}{3}) (32.000)$$

$$= 12.0107.$$

c. Molal Heat Capacity

At $t_1 = 18°C.$,

$$C'_{P(H_2)} = 6.88 \underline{1/} \text{ cal/(gm mole)(°K)};$$

$$C'_{p_{(O_2)}} = 7.01 \underline{1/} \text{ cal/(gm mole)(°K)};$$

$$C_{p_1} = X'_{H_2} C'_{p_{(H_2)}} + X'_{O_2} C'_{p_{(O_2)}}$$

$$= (2/3)(6.88) + (1/3)(7.01) = 6.9233.$$

d. Specific Heat Ratio

$$\gamma_1 = \frac{C_{p_1}}{C_{p_1} - R} = \frac{6.9233}{6.9233 - 1.98719} = 1.4026.$$

e. Heat of Formation $\Delta H'_{f(i)}$ of Each Reactant at the Initial Conditions

By definition of $\Delta H'_{f(i)}$, the heat of formation of an element (in its standard state of aggregation) at t_1 is equal to zero.

Therefore,

$$\Delta H'_{f_{(H_2)}} = 0.0;$$

$$\Delta H'_{f_{(O_2)}} = 0.0.$$

Step 9. Initial Assumption for p_2

$$p_2 = 20.00 \text{ atmos.}$$

Step 10. Initial Assumption for T_2

$$T_2 = 3800° K.$$

Step 11. Determination of Numerical Values of the Equilibrium Constants for the Dissociation Reactions

From Figures 12 through 15,

$$K_{p_{(H_2O)}} = .3758 \text{ (atmos)}^{1/2} \text{ at } T_2 = 3800° K., *$$

$$K'_{p_{(H_2O)}} = .5984 \text{ (atmos)}^{1/2} \text{ at } T_2 = 3800° K., **$$

---

* This value also obtainable from Ref. 8, Table 4, by graphical interpolation.
** This value also given in Ref. 7, page 25.

$$K_{p_{(H_2)}} = 1.107 \ (\text{atmos})^{1/2} \quad \text{at } T_2 = 3800°K., *$$

$$K_{p_{(O_2)}} = 1.032 \ (\text{atmos})^{1/2} \quad \text{at } T_2 = 3800°K. **$$

Step 12. Calculation of the Partial Pressures (p_j's) in the Final Mixture

Referring to equations (114) and (115), let

$$c_{11} = \left(\frac{K_{p_{(H_2O)}}}{p_{H_2}} \right)^2, \tag{116}$$

$$c_{12} = \left(\frac{K_{p_{(O_2)}} \ K_{p_{(H_2O)}}}{p_{H_2}} + \frac{K'_{p_{(H_2O)}}}{p_{H_2}^{\frac{1}{2}}} + 1 \right), \tag{117}$$

$$c_{13} = \left(p_{H_2} + K_{p_{(H_2)}} \ p_{H_2}^{\frac{1}{2}} - p_2 \right), \tag{118}$$

$$k_{11} = 2 \left(\frac{K_{p_{(H_2O)}}}{p_{H_2}} \right)^2 = 2 \ c_{11}, \tag{119}$$

$$k_{12} = \left(\frac{K_{p_{(O_2)}} \ K_{p_{(H_2O)}}}{p_{H_2}} + \frac{K'_{p_{(H_2O)}}}{2 \cdot p_{H_2}^{\frac{1}{2}}} \right), \tag{120}$$

and

$$k_{13} = - \left(p_{H_2} + \frac{1}{2} K_{p_{(H_2)}} \ p_{H_2}^{\frac{1}{2}} \right). \tag{121}$$

Then, from equation (114),

$$p_{H_2O} = \frac{- c_{12} \pm \sqrt{c_{12}^2 - 4 c_{11} \ c_{13}}}{2 c_{11}}, \tag{122}$$

* This value also given in Ref. 7, page 25.
** This value also given in Ref. 6.

and, from equation (115),

$$p_{H_2O} = \frac{-k_{12} \pm \sqrt{k_{12}^2 - 4k_{11}\, k_{13}}}{2k_{11}} \tag{123}$$

For the solution of equations (122) and (123), values of p_{H_2} have been assumed, as indicated in Table 1. These values of p_{H_2}, in conjunction with the values of the equilibrium constants (Step 11) and the assumed final pressure (Step 9) have been used to determine the values of the constants c_{11}, c_{12}, c_{13}, and k_{11}, k_{12}, k_{13} (Equations (116) through (121)). Equations (122) and (123) were then solved to obtain two values of p_{H_2O}, indicated in Table 1 as p_{H_2O} (Equation (122)) and p_{H_2O} (Equation (123)). The difference between these two values of p_{H_2O} is designated in Table 1 as Δp_{H_2O}. The values of Δp_{H_2O} obtained were plotted as a function of the assumed p_{H_2} (Figure 20). After two trials (i.e., two assumed values of p_{H_2}), the value of p_{H_2} at the point where the curve crossed the $\Delta p_{H_2O} = 0$ line, was taken as the assumed p_{H_2} for the following trial. The fourth trial gave sufficiently accurate values of p_{H_2} and p_{H_2O} to satisfy both equations (122) and (123). (An alternate method of obtaining a solution of the simultaneous equations (122) and (123) is to plot each of these two equations as p_{H_2} vs p_{H_2O} on the same graph and determine the point of intersection of the two curves. It may be found that in some cases more rapid convergence is obtained by this method.)

TABLE 1

Calculation of p_{H_2} and p_{H_2O} from equations (122) and (123)

$p_2 = 20$ atmos

$T_2 = 3800°K;$ $K_{p_{(H_2O)}} = .3758 \text{ (atmos)}^{\frac{1}{2}};$ $K'_{p_{(H_2O)}} = .5984 \text{ (atmos)}^{\frac{1}{2}};$

$K_{p_{(H_2)}} = 1.107 \text{ (atmos)}^{\frac{1}{2}};$ $K_{p_{(O_2)}} = 1.032 \text{ (atmos)}^{\frac{1}{2}}.$

	Trial 1	Trial 2	Trial 3	Trial 4
p_{H_2}	4.35	3.00	3.43	3.51
c_{11}	.0074634	.0156918	.012003	.0114640
c_{12}	1.37607	1.47476	1.4362	1.42989
c_{13}	-13.3412	-15.0826	-14.520	-14.4160
k_{11}	.0149268	.0313836	.024006	.022928
k_{12}	.232611	.302019	.27463	.270193
k_{13}	-5.50442	-3.95870	-4.4551	-4.54698
p_{H_2O} (Eq. (122))	9.23306	9.30578	9.3768	9.3733
p_{H_2O} (Eq. (123))	12.9320	7.4068	9.0550	9.3732
Δp_{H_2O}	+3.6989	-1.8990	-.3218	-.0001

Using equations (106) through (109), respectively, to calculate the values of the partial pressures of the remaining four constituents,

$$p_{O_2} = \left(\frac{K_{p_{(H_2O)}} \, p_{H_2O}}{p_{H_2}^2}\right)^2 = \left[\frac{(.3758)(9.3732)}{3.51}\right]^2 \approx 1.00710 \text{ atmos,}$$

$$p_{OH} = \frac{K'_{p_{(H_2O)}} \, p_{H_2O}}{p_{H_2}^{\frac{1}{2}}} = \frac{(.5984)(9.3732)}{(3.51)^{1/2}} \approx 2.99382 \text{ atmos,}$$

$$p_H = K_{p_{(H_2)}} \, p_{H_2}^{\frac{1}{2}} = (1.107)(3.51)^{\frac{1}{2}} = 2.07396 \text{ atmos,}$$

$$p_O = \frac{K_{p_{(O_2)}} K_{p_{(H_2O)}} \, p_{H_2O}}{p_{H_2}} = \frac{(1.032)(.3758)(9.3732)}{3.51} = 1.03566 \text{ atmos.}$$

Rounding off to three decimal places all of the values of partial pressure obtained above, and adjusting the largest of these values (p_{H_2O}) slightly in order to give a total (p_2) of 20.000, the following values of partial pressure $(p_j's)$ are obtained:

$$p_{H_2} \approx 3.510 \text{ atmos}$$

$$p_{H_2O} \approx 9.379$$

$$p_{O_2} \approx 1.007$$

$$p_{OH} = 2.994$$

$$p_H \approx 2.074$$

$$p_O \approx 1.036$$

$$\sum_j p_j \approx p_2 \approx 20.000 \text{ atmos}$$

Step 13.   Total Number of Moles of the Final Mixture

Using equation (75),

$$n_2 = p_2 \frac{\sum_i n'_i M_{w(i)}}{\sum_j p_j M_{w(j)}}$$

$$= p_2 \left[\frac{n'_{H_2} M_{w(H_2)} + n'_{O_2} M_{w(O_2)}}{p_{H_2O} M_{w(H_2O)} + p_{H_2} M_{w(H_2)} + p_{O_2} M_{w(O_2)} + p_{OH} M_{w(OH)} + p_H M_{w(H)} + p_O M_{w(O)}} \right]$$

$$= 20.000 \left[\frac{(1)(2.0160) + (.5)(32.0000)}{(9.379)(18.0160) + (3.510)(2.0160) + (1.007)(32.0000) + (2.994)(17.0080) + (2.074)(1.0080) + (1.036)(16.000)} \right]$$

or $\qquad n_2 = 1.29676$.

Step 14. Composition of the Final Mixture

Using equation (73) and values of p_j calculated in Step 12,

$$n_{H_2O} = \frac{p_{H_2O}}{p_2} n_2 = \frac{(9.379)(1.29676)}{20.000} \qquad = .608116$$

$$n_{H_2} = \frac{p_{H_2}}{p_2} n_2 = \frac{(3.510)(1.29676)}{20.000} \qquad = .227581$$

$$n_{O_2} = \frac{p_{O_2}}{p_2} n_2 = \frac{(1.007)(1.29676)}{20.000} \qquad = .065292$$

$$n_{OH} = \frac{p_{OH}}{p_2} n_2 = \frac{(2.994)(1.29676)}{20.000} \qquad = .194125$$

$$n_H = \frac{p_H}{p_2} n_2 = \frac{(2.074)(1.29676)}{20.000} \qquad = .134474$$

$$n_O = \frac{p_O}{p_2} n_2 = \frac{(1.036)(1.29676)}{20.000} \qquad = .067172$$

$$\sum_j n_j = n_2 \qquad = 1.29676$$

Step 15. Properties of the Final Mixture

a. Mole Fractions

$$X_{H_2O} = \frac{n_{H_2O}}{n_2} = \frac{p_{H_2O}}{p_2} = \frac{9.379}{20.000} = .46895$$

$$X_{H_2} = \frac{n_{H_2}}{n_2} = \frac{p_{H_2}}{p_2} = \frac{3.510}{20.000} = .17550$$

$$X_{O_2} = \frac{n_{O_2}}{n_2} = \frac{p_{O_2}}{p_2} = \frac{1.007}{20.000} = .05035$$

$$X_{OH} = \frac{n_{OH}}{n_2} = \frac{p_{OH}}{p_2} = \frac{2.994}{20.000} = .14970$$

$$X_H = \frac{n_H}{n_2} = \frac{p_H}{p_2} = \frac{2.074}{20.000} = .10370$$

$$X_O = \frac{n_O}{n_2} = \frac{p_O}{p_2} = \frac{1.036}{20.000} = .05180$$

$$\sum_j x_j = 1.00000$$

b. Molecular Weight

$$
\begin{aligned}
M_{W_2} &= \sum_j x_j \, M_{W(j)} \\
&= X_{H_2O} \, M_{W(H_2O)} + X_{H_2} \, M_{W(H_2)} + X_{O_2} \, M_{W(O_2)} \\
&\quad + X_{OH} \, M_{W(OH)} + X_H \, M_{W(H)} + X_O \, M_{W(O)}
\end{aligned}
$$

$$
\begin{aligned}
&= (.46895)(18.0160)+(.17550)(2.0160) \\
&\quad + (.05035)(32.0000)+(.14970)(17.0080) \\
&\quad + (.10370)(1.0080)+(.05180)(16.0000),
\end{aligned}
$$

or

$$M_{W_2} = 13.8930.$$

c. Molal Heat Capacity*

At $T_2 = 3800°K$,

$$C_{p(H_2O)} = 13.87 \text{ cal/(gm mole)}(°K),$$

$$C_{p(H_2)} = 9.10 \text{ cal/(gm mole)}(°K),$$

$$C_{p(O_2)} = 9.85 \text{ cal/(gm mole)}(°K),$$

---

* The molal heat capacities for H_2O, H_2, O_2 and OH were obtained from Figure 16 through 19, respectively; and the values for O and H were calculated from enthalpy data given in Ref. 7, page 22.

$$C_{p_{(OH)}} = 9.115 \text{ cal/(gm mole)}(°K),$$

$$C_{p_{(H)}} = 4.965 \text{ cal/(gm mole)}(°K),$$

$$C_{p_{(O)}} = 4.965 \text{ cal/(gm mole)}(°K).$$

$$C_{p_2} = \sum_j x_j \, C_{p_{(j)}}$$

$$= x_{H_2O} \, C_{p_{(H_2O)}} + x_{H_2} \, C_{p_{(H_2)}} + x_{O_2} \, C_{p_{(O_2)}} + x_{OH} \, C_{p_{(OH)}}$$

$$+ x_H \, C_{p_{(H)}} + x_O \, C_{p_{(O)}}$$

$$= (.46895)(13.87) + (.17550)(9.10) + (.05035)(9.85)$$
$$+ (.14970)(9.115) + (.10370)(4.965) + (.05180)(4.965),$$

or

$$C_{p_2} = 10.7339 \text{ cal/(gm mole)}(°K).$$

d. Specific Heat Ratio

$$\gamma_2 = \frac{C_{p_2}}{C_{p_2} - R} = \frac{10.7339}{10.7339 - 1.98719} = 1.2272.$$

e. Heat of Formation $\Delta H'_{f_{(j)}}$, of Each Product at the Initial Temperature*

By definition of $\Delta H'_{f_{(j)}}$, in the same manner as in Step 8 for the

initial mixture, the heat of formation of an element (in its standard state of aggregation) at t_1 is equal to zero. Therefore,

$$\Delta H'_{f_{(H_2)}} = 0.0,$$

$$\Delta H'_{f_{(O_2)}} = 0.0.$$

From the literature, at $t_L = 18°C$,

$$\Delta H_{f_{L \, (H_2O)}} = +57,801** \text{ cal/gm mole,}$$

but, since $t_L = t_1$ in this case,

$$\Delta H'_{f \, (H_2O)} = \Delta H_{f_{L \, (H_2O)}} = +57,801 \text{ cal/gm mole.}$$

---

* See footnote in Step 8, par. e.
** Ref. 2, page 255.

From the literature, at $t_L = 25°C$,

$$\Delta H_{f_L (OH)} = -9,310^* \text{ cal/gm mole,}$$

$$\Delta H_{f_L (H)} = -51,900^* \text{ cal/gm mole,}$$

$$\Delta H_{f_L (O)} = -59,100^* \text{ cal/gm mole,}$$

but, since $t_L \neq t_1$ in this case, Equation (81) is used to calculate values of $\Delta H'_{f(j)}$ for OH, H and O**:

$$\Delta H'_{f(j)} = \Delta H_{f_L(j)} - H'_j + \sum H'_{e(j)} . \tag{81}$$

Values of H'_j and $\sum H'_{e(j)}$ obtained from the literature for OH, H and O are indicated in Table 2.

From the above data and equation (81),

$$\Delta H'_{f(OH)} = \Delta H_{f_L (OH)} - H'_{(OH)} + \sum H'_{e(OH)}$$

$$= -9,310 + 47.9 - 48.5 = -9310.6 \text{ cal/gm mole;}$$

$$\Delta H'_{f(H)} = \Delta H_{f_L (H)} - H'_{(H)} + \sum H'_{e(H)}$$

$$= -51,900 + 33.2 - 24.0 = -51,890.8 \text{ cal/gm mole;}$$

$$\Delta H'_{f(O)} = \Delta H_{f_L(O)} - H'_{(O)} + \sum H'_{e(O)}$$

$$= -59,100 + 33.2 - 24.5 = -59,091.3 \text{ cal/gm mole.}$$

---

* Ref. 7, page 26.
** The difference between $\Delta H'_{f(j)}$ and $\Delta H_{f_L (j)}$ for this case $(t_L - t_1 = 7°C)$ is negligible ($<0.1\%$). The calculation of $\Delta H'_{f(j)}$ according to equation (81) has been included for purpose of illustration.

TABLE 2

Literature Values of Enthalpies, cal/gm mole of "j"

Component "j"	H'_j (cal/gm mole)	$\sum H'_{e(j)}$ (cal/gm mole of "j")	Reference
OH	-47.9	-48.5	Calculated (*) from
H	-33.2	-24.0	data in Ref. 7,
O	-33.2	-24.5	page 22 and Ref. 2,
			page 216.

* The calculation of H'_j and $\sum H'_{e(j)}$ from data obtained in References 2 and 7 is shown below for OH.

$$H'_{(OH)} = \int_{T_L}^{T_1} \left(\frac{dH}{dT}\right)_{(OH)} dT = \int_{T_L}^{T_1} C_{p_{(OH)}} dT \cong \bar{C}_{p_{(OH)}} \left(T_1 - T_L\right) , \qquad (124)$$

where $\bar{C}_{p_{(OH)}}$ = mean C_p between T_L (298°K) and T_1 (291°K) = 6.8421 $\frac{cal}{(gm\ mole)(°K)}$; therefore, $H'_{(OH)}$ = (6.8421)(291-298) = -47.9 cal/gm mole.

The formation reaction for one mole of OH is 1/2 H_2 + 1/2 $O_2 \longrightarrow$ OH; then,

$$\sum H'_{e(OH)} = n_{H_2} \bar{C}_{p_{(H_2)}} \left(T_1 - T_L\right) + n_{O_2} \bar{C}_{p_{(O_2)}} \left(T_1 - T_L\right) ,$$

where $\bar{C}_{p_{(H_2)}}$ = mean C_p between T_L (298°K) and T_1 (291°K) = 6.86 cal/(gm mole)(°K), and $\bar{C}_{p_{(O_2)}}$ = mean C_p between T_L (298°K) and T_1 (291°K) = 7.00 cal/(gm mole)(°K);

$$\sum H'_{e(OH)} = (1/2)(6.86)(291-298)+1/2(7.00)(291-298) = -48.5 \frac{cal}{gm\ mole\ of\ OH} .$$

The values of the heats of formation, $\Delta H'_{f(j)}$, calculated above, are summarized for convenience in Table 3.

TABLE 3

Heats of Formation of Products, cal/gm mole

$\Delta H'_{f(H_2)}$	$\Delta H'_{f(O_2)}$	$\Delta H'_{f(H_2O)}$	$\Delta H'_{f(OH)}$	$\Delta H'_{f(H)}$	$\Delta H'_{f(O)}$
0.0	0.0	+57,801	-9310.6	-51,890.8	-59,091.3

Step 16.   Heat of Reaction, Energy Release per Mole of Initial Mixture

Using data from Step 14 and Step 15 (par. e),

$$\sum_j n_j \Delta H'_{f(j)} = n_{H_2O}\Delta H'_{f(H_2O)} + n_{H_2}\Delta H'_{f(H_2)} + n_{O_2}\Delta H'_{f(O_2)} + n_{OH}\Delta H'_{f(OH)} + n_H\Delta H'_{f(H)} + n_O \Delta H'_{f(O)}$$

$$= (.608116)(+57,801) + (.227581)(0.0) + (.065292)(0.0)$$
$$+ (.194125)(-9310.6) + (.134474)(-51,890.8) + (.067172)$$
$$(-59,091.3)$$

$$= +22,395.0 \text{ calories;}$$

$$\sum_i n'_i \Delta H'_{f(i)} = n'_{H_2} \Delta H'_{f(H_2)} + n'_{O_2} \Delta H'_{f(O_2)}$$

$$= (1)(0.0) + (1/2)(0.0) = 0;$$

$$n_1 = n'_{H_2} + n'_{O_2} = 1 + \tfrac{1}{2} = 1.5 \text{ moles ,}$$

then, by equation (83),

$$\Delta H_R = \frac{\sum_j n_j \Delta H'_{f(j)} - \sum_i n'_i \Delta H'_{f(i)}}{n_1} = \frac{+22,395.0 - 0.0}{1.5} ,$$

or $\Delta H_R = +14,930.0$ cal/gm mole of initial mixture.

Step 17.   Energy Release Function

Using equation (84) and data from Steps 7, 8 (par. d) and 16,

$$B = \frac{\Delta H_R}{\gamma_1 R T_1} = \frac{+14,930.0}{(1.4026)(1.9871\,9)(291)} = 18.407.$$

Step 18. Gamma Ratio

From Figure 5 and data from Steps 8 (par. d.) and 15 (par. d.) or by direct calculation,

$$\frac{\gamma_2}{\gamma_1} = \frac{1.2272}{1.4026} = .87495 .$$

Step 19. Molecular Weight Ratio

Using data from Steps 8 (par. b) and 15 (par. b),

$$\frac{M_{w_2}}{M_{w_1}} = \frac{13.8930}{12.0107} = 1.15672 .$$

Step 20. The Dimensionless Parameter E

From Figure 1 and data from Steps 15 (par. d) and 17, or using equation (47),

$$E = (\gamma_2^2 - 1)B = \left[(1.2272)^2 - 1\right]\left[18.407\right] = 9.31431 .$$

Step 21. Gamma Function

From Figure 2 and data from Steps 8 (par. d) and 15 (par. d), or using equation (48),

$$\Gamma = \frac{\gamma_2^2 - \gamma_1}{\gamma_1(\gamma_1 - 1)} = \frac{(1.2272)^2 - 1.4026}{1.4026(1.4026 - 1)} = 0.183146 .$$

Step 22. Pseudo-Mach Number (Squared)

From Figure 3 and data from Steps 20 and 21, or using equation (45),

$$\overline{M}_1^2 = 2E + 2\Gamma = (2)(9.31431) + 2(0.183146) = 18.99491 .$$

Step 23. Mach Number (Squared)

From Figure 4, and values of $\overline{M}_1^2$ and $\frac{\gamma_2}{\gamma_1}$ from Steps 18 and 22,

$M_1^2 = 19.0$ (Same as $\overline{M}_1^2$ within the accuracy of reading Figure 4).

Step 24. The Dimensionless Parameter $\gamma_1 M_1^2$

From Figure 9 and data from Steps 8 (par. d) and 23, or by direct calculation,

$$\gamma_1 M_1^2 = (1.4026)(19.0) = 26.65 .$$

Step 25. Temperature - Molecular Weight Ratio

From Figure 8 and data from Steps 15 (par. d) and 24, or using equation (85),

$$\frac{T_2 \, M_{W_1}}{T_1 \, M_{W_2}} = \frac{\gamma_2}{(\gamma_2 + 1)^2} \left(\gamma_1 M_1^2 + \frac{1}{\gamma_1 M_1^2} + 2 \right)$$

$$= \frac{1.2272}{(1.2272+1)^2} \left(26.65 + \frac{1}{26.65} + 2 \right)$$

$$= 7.0972 .$$

Step 26. Final Temperature

Using data from Steps 7, 19 and 25,

$$T_2 = \frac{T_2 M_{w_1}}{T_1 M_{w_2}} \cdot \frac{M_{w_2}}{M_{w_1}} \cdot T_1$$

$$= (7.0972)(1.15672)(291)$$

$$= \underline{2389°K} .$$

Since this calculated value of T_2 did not check the assumed value (Step 10), other values of T_2 were assumed and Steps 10 through 26 were repeated until sufficient data were obtained to permit graphical determination of the correct value of T_2 corresponding to the assumed pressure.

A plot of Δp_{H_2O} vs p_{H_2} (assumed) for each assumed T_2 is shown in Figure 21, and a plot of T_2 (calculated) vs T_2 (assumed) is shown in Figure 22 (For Trials 1 through 29, i.e., for p_2 (assumed) = 20.00 atmos). Table 4 lists principal intermediate values calculated in these trials.

The correct value of T_2 corresponding to the first assumed p_2 of 20.00 atmos is shown in Figure 22 to be 3565°K (the point of intersection of the curve with the 45° line). This value of T_2 is also indicated in Table 4 (Trials 25-29) as T_2 (adjusted).

It was considered that the value of $T_{2(adjusted)}$ obtained in Trial 29 as described above was so close to the value of $T_{2(assumed)}$ that further calculations were not warranted. This was considered to be justifiable since the thermodynamic data (K_p and C_p) available were not of sufficient accuracy to give data different from that obtained in the last trial (Trial 29). Hence, all intermediate values calculated in the last trial (Trial 29), based on the assumed T_2 for that trial, for all practical purposes can be considered to be accurate values corresponding to the adjusted T_2.

Step 27. Pressure Ratio

Using the values of γ_2 and $\gamma_1 M_1^2$ from Trial 29, then from Figure 6 or using equation (87),

$$\frac{P_2}{P_1} = \frac{1}{\gamma_2 + 1} (\gamma_1 M_1^2 + 1)$$

$$= \frac{1}{1.20714 + 1} (37.3793 + 1)$$

$$= 17.3887 .$$

Step 28. Final Pressure

Using data from Steps 6 and 27,

$$P_2 = \frac{P_2}{P_1} \cdot P_1 = (17.3887)(1) = 17.3887 \text{ atmos.}$$

Since this calculated value of p_2 did not check the assumed value (Step 9), other values of p_2 were assumed and Steps 9 through 28 were repeated until sufficient data were obtained to permit graphical determination of the correct value of p_2.

A plot of Δp_{H_2O} vs $p_{H_2(assumed)}$ for each assumed T_2 is shown in Figures 21, 23, 25, 26 for assumed p_2's of 20, 17, 17.17 and 17.20, respectively. A plot of $T_{2(calculated)}$ vs $T_{2(assumed)}$ is shown in Figures 22, 24 and 27 for assumed p_2's of 20, 17 and 17.20, respectively*.

---

* For an assumed p_2 of 17.17, no plot of $T_{2(calculated)}$ vs $T_{2(assumed)}$ was necessary since the calculated T_2 for the first trial was so close to the assumed T_2 that additional trials were not warranted.

Figure 28 shows a plot of $P_{2(calculated)}$ vs $P_{2(assumed)}$. Table 4 lists principal intermediate values calculated in Trials 1 through 53.

The correct value of the final detonation pressure, p_2, is shown in Figure 28 to be 17.22 atmos (the point of intersection of the curve with the 45° line). This value of p_2 is also indicated as $P_{2(adjusted)}$ in Table 4.

It was considered that the value of $P_{2(adjusted)}$ obtained in Trial 53 as described above was so close to the value of $P_{2(assumed)}$ that further calculations were not warranted. Hence, all intermediate values calculated in the last trial (Trial 53), based on the assumed p_2 for that trial, can be considered to be accurate values corresponding to the adjusted p_2.

Step 29.   Detonative Mach Number

Using the value of M_1^2 from Trial 53,

$$M_1 = \sqrt{M_1^2} = \sqrt{26.40} = 5.13809 .$$

Step 30.   Detonation Velocity

Using equation (89) and data from Steps 7, 8 (pars. b and d) and 29,

$$D = M_1 \sqrt{\frac{J \gamma_1 R T_1}{M_{w_1}}}$$

$$= 5.13809 \sqrt{\frac{(4.185 \times 10^7)(1.4026)(1.98719)(291)}{12.0107}}$$

$$= 2.73149 \times 10^5 \text{ cm/sec.}$$

This detonation velocity expressed in more common units is

2731.5 meters/sec

or

8961.6 ft/sec .

Step 31.   Calculation of Additional Data

a. Density Ratio

Using the values of $\dfrac{P_2}{P_1}$ and $\dfrac{T_2 M_{w_1}}{T_1 M_{w_2}}$ from Trial 53,

then from Figure 10 or using equation (15),

$$\frac{\rho_2}{\rho_1} = \frac{P_2}{P_1} \bigg/ \frac{T_2 M_{w_1}}{T_1 M_{w_2}} = \frac{17.2269}{9.67764} = 1.78007 \ .$$

b. Initial Density

Using equation (90) and the values of P_1, T_1 and M_{w_1} from Steps 6, 7 and 8 (par. b) of this sample calculation,

$$\rho_1 = \frac{M_{w_1} P_1}{J R T_1} = \frac{(12.0107)(1.0133 \times 10^6)}{(4.185 \times 10^7)(1.98719)(291)} = 5.02895 \times 10^{-4} \, gm/cm^3,$$

or initial density is 0.5029 gm/liter.

c. Final Density

Using the above values of $\dfrac{\rho_2}{\rho_1}$ and ρ_1 ,

$$\rho_2 = \frac{\rho_2}{\rho_1} \cdot \rho_1 = (1.78007)(5.02895 \times 10^{-4})$$

$$= 8.95188 \times 10^{-4} \, gm/cm^3,$$

or final density is 0.8952 gm/liter.

a. **Density Ratio**

Using the values of $\dfrac{P_2}{P_1}$ and $\dfrac{T_2 M_{w_1}}{T_1 M_{w_2}}$ from Trial 53,

then from Figure 10 or using equation (15),

$$\frac{\rho_2}{\rho_1} \doteq \frac{P_2}{P_1} \bigg/ \frac{T_2 M_{w_1}}{T_1 M_{w_2}} = \frac{17.2269}{9.67764} = 1.78007 \ .$$

b. **Initial Density**

Using equation (90) and the values of P_1, T_1 and M_{w_1} from

Steps 6, 7 and 8 (par. b) of this sample calculation,

$$\rho_1 = \frac{M_{w_1} P_1}{J R T_1} = \frac{(12.0107)(1.0133 \times 10^6)}{(4.185 \times 10^7)(1.98719)(291)} = 5.02895 \times 10^{-4} \, \text{gm/cm}^3,$$

or initial density is 0.5029 gm/liter.

c. **Final Density**

Using the above values of $\dfrac{\rho_2}{\rho_1}$ and ρ_1,

$$\rho_2 = \frac{\rho_2}{\rho_1} \cdot \rho_1 = (1.78007)(5.02895 \times 10^{-4})$$

$$= 8.95188 \times 10^{-4} \, \text{gm/cm}^3,$$

or final density is 0.8952 gm/liter.

APPENDIX IV

GRAPHS

FIGURE I. DIMENSIONLESS PARA-
METER EPSILON VERSUS
THE ENERGY RELEASE
FUNCTION, ($\mathbb{E}$ vs $\mathbb{B}$).

$$\mathbb{E} = (\delta_2^2 - 1)\mathbb{B}.$$

$$\Gamma = \frac{\delta_2^2 - \delta_1}{\delta_1 (\delta_2 - 1)}$$

FIGURE 2. THE GAMMA FUNCTION VERSUS THE SQUARE OF THE FINAL SPECIFIC HEAT RATIO, (Γ vs δ_2^2 FOR $\Gamma = -1$ TO $+4$).

$$\bar{M}_i^2 = 2B + 2\Gamma$$

$\Gamma = +1.0$
+0.5
0
-0.5
-1.0

FIGURE 3. THE SQUARE OF THE PSEUDO-MACH NUMBER VERSUS THE DIMENSIONLESS PARAMETER (EPSILON), ($\bar{M}_i^2$ vs B).

$$\overline{M}_1^2 = M_1^2 \div \left(\frac{\xi_3}{\xi_1}\right)^2$$

$$\overline{M}_1^2 = M_1^2 \left(\frac{\xi_3}{\xi_1}\right)^2$$
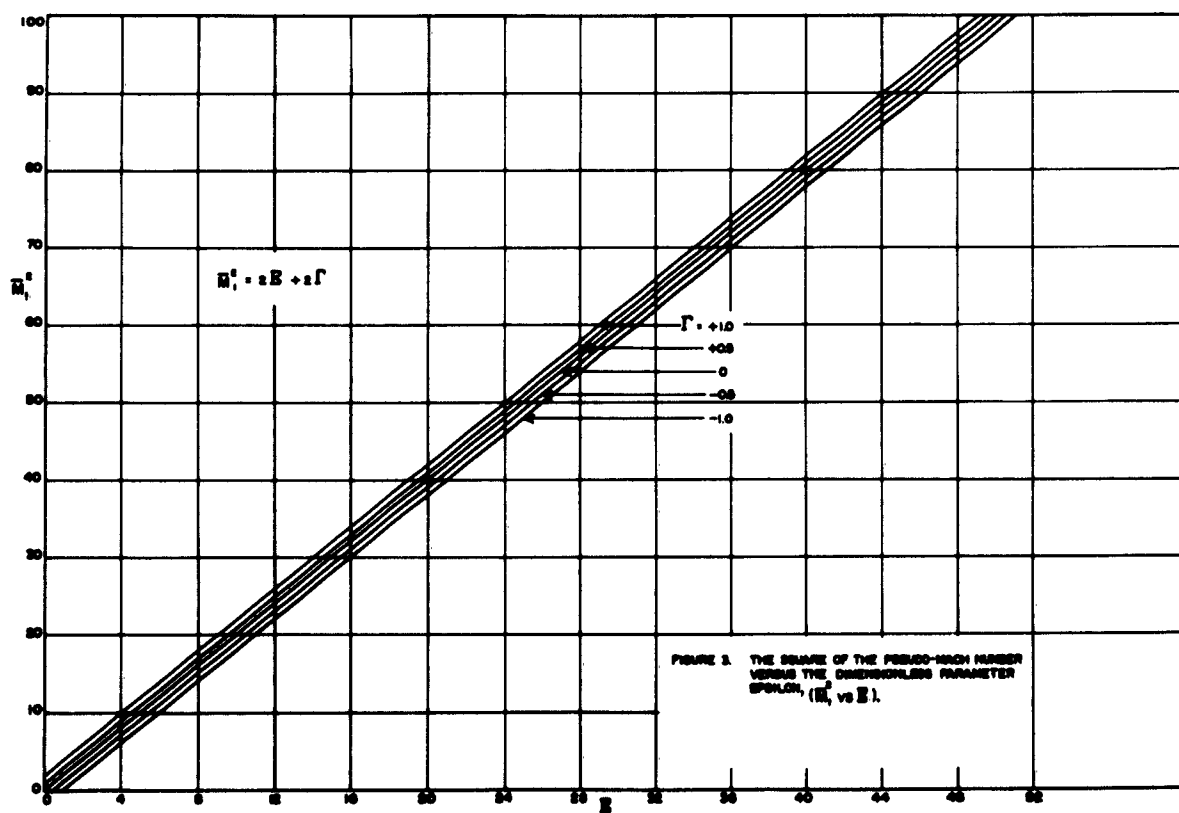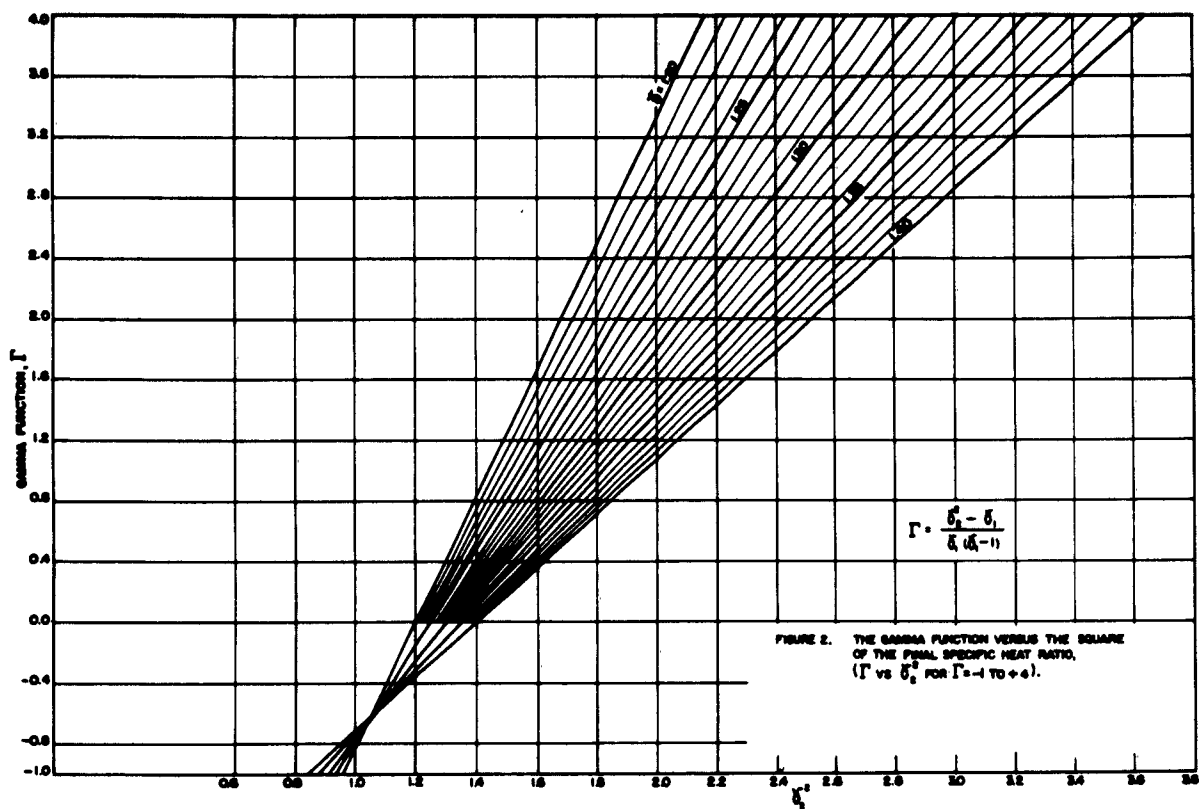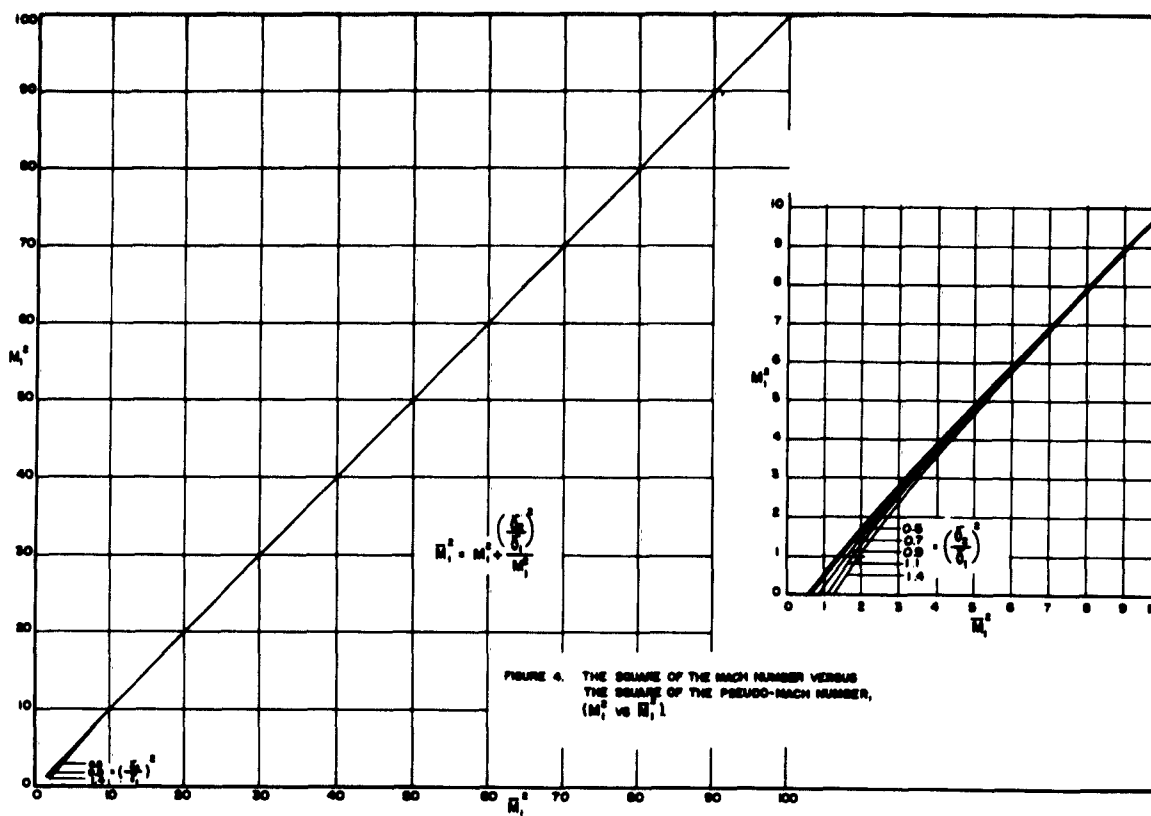
FIGURE 4. THE SQUARE OF THE MACH NUMBER VERSUS
THE SQUARE OF THE PSEUDO-MACH NUMBER,
$(M_1^2 \text{ vs } \overline{M}_1^2)$
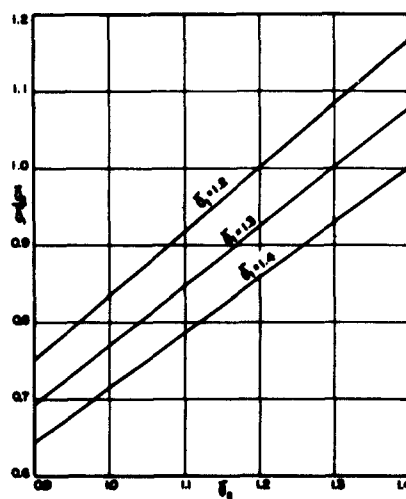
FIGURE 5. THE GAMMA RATIO VERSUS THE FINAL SPECIFIC HEAT RATIO,
$\left(\frac{\overline{\gamma}}{\gamma} \text{ vs } \xi_3\right)$

FIGURE 9. THE SQUARE OF THE MACH NUMBER
VERSUS THE TERM $\xi \, (M)^2$.
$(M)^2$ vs $\xi \, (M)^2$

$\dfrac{\rho}{\rho_t} = \dfrac{P}{P_t} \cdot \dfrac{T_t}{T}$

FIGURE 10. THE DENSITY RATIO VERSUS
THE PRESSURE RATIO.
$\left(\dfrac{\rho}{\rho_t} \text{ vs } \dfrac{P}{P_t} \right)$

FIGURE 11. TYPICAL PLOT FOR BEING CONVERGENCE IN TRIAL-AND-ERROR
SOLUTIONS. (SEE FULL VON RENDERING)

FIGURE 12. EQUILIBRIUM CONSTANT DATA FOR
THE REACTION, $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$.

$(K_{p(H_2O)}$ vs T)

(DATA OBTAINED FROM REF. 7, P.24)

$$K_{p(H_2O)} = \frac{(P_{H_2})(P_{O_2})^{\frac{1}{2}}}{P_{H_2O}}$$

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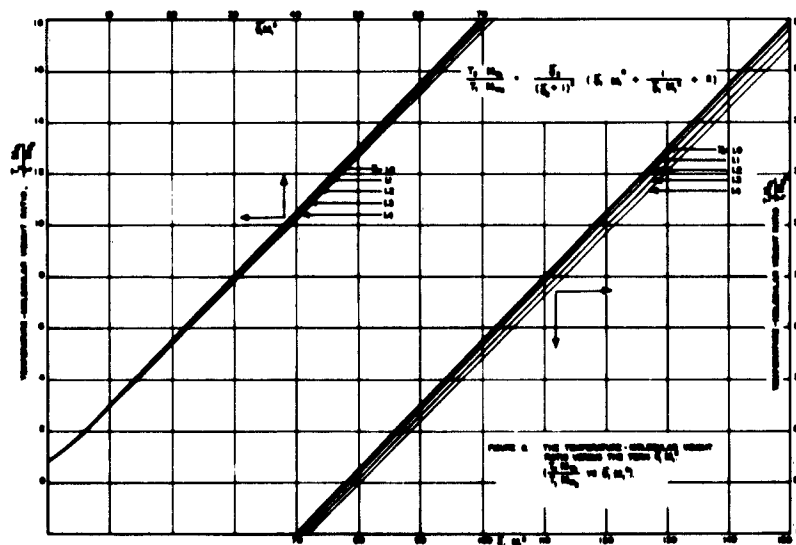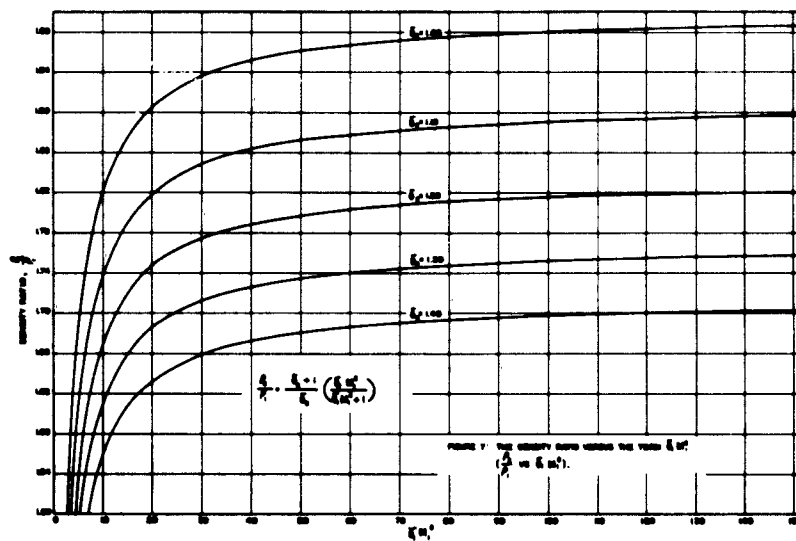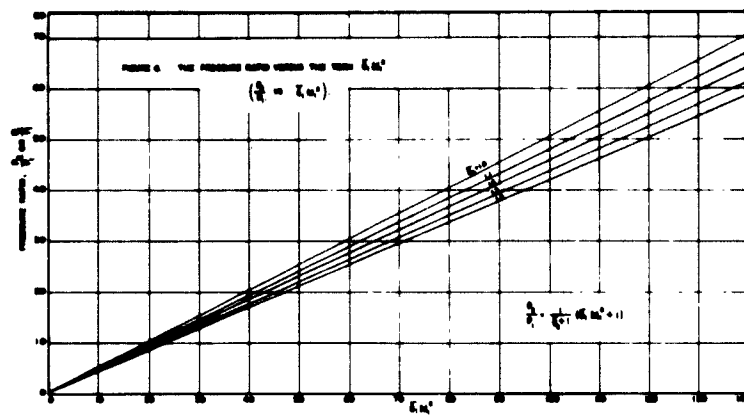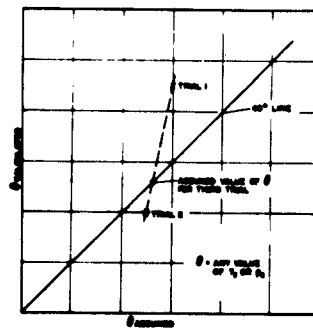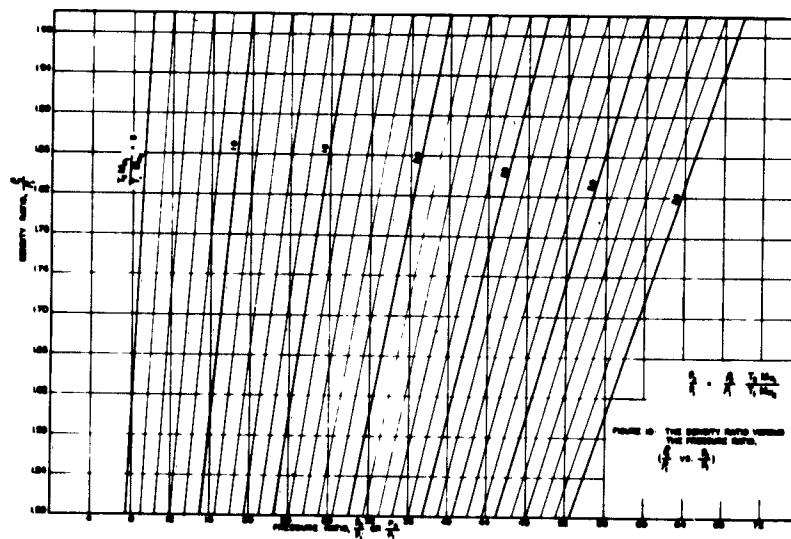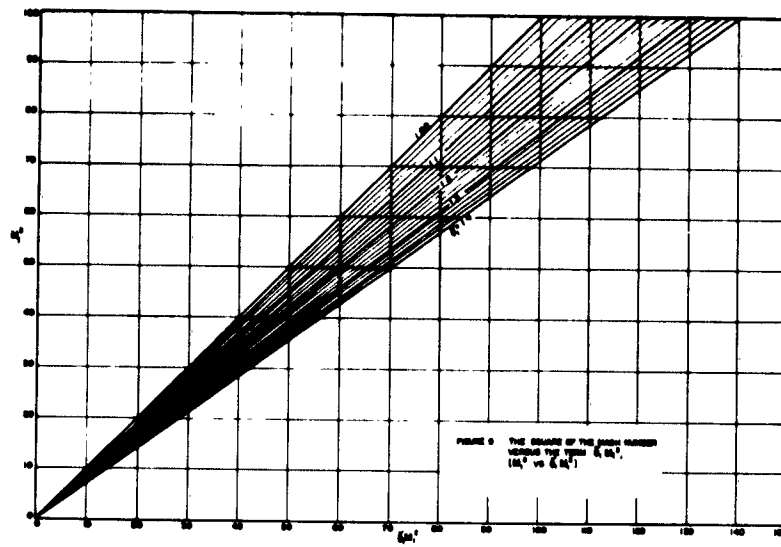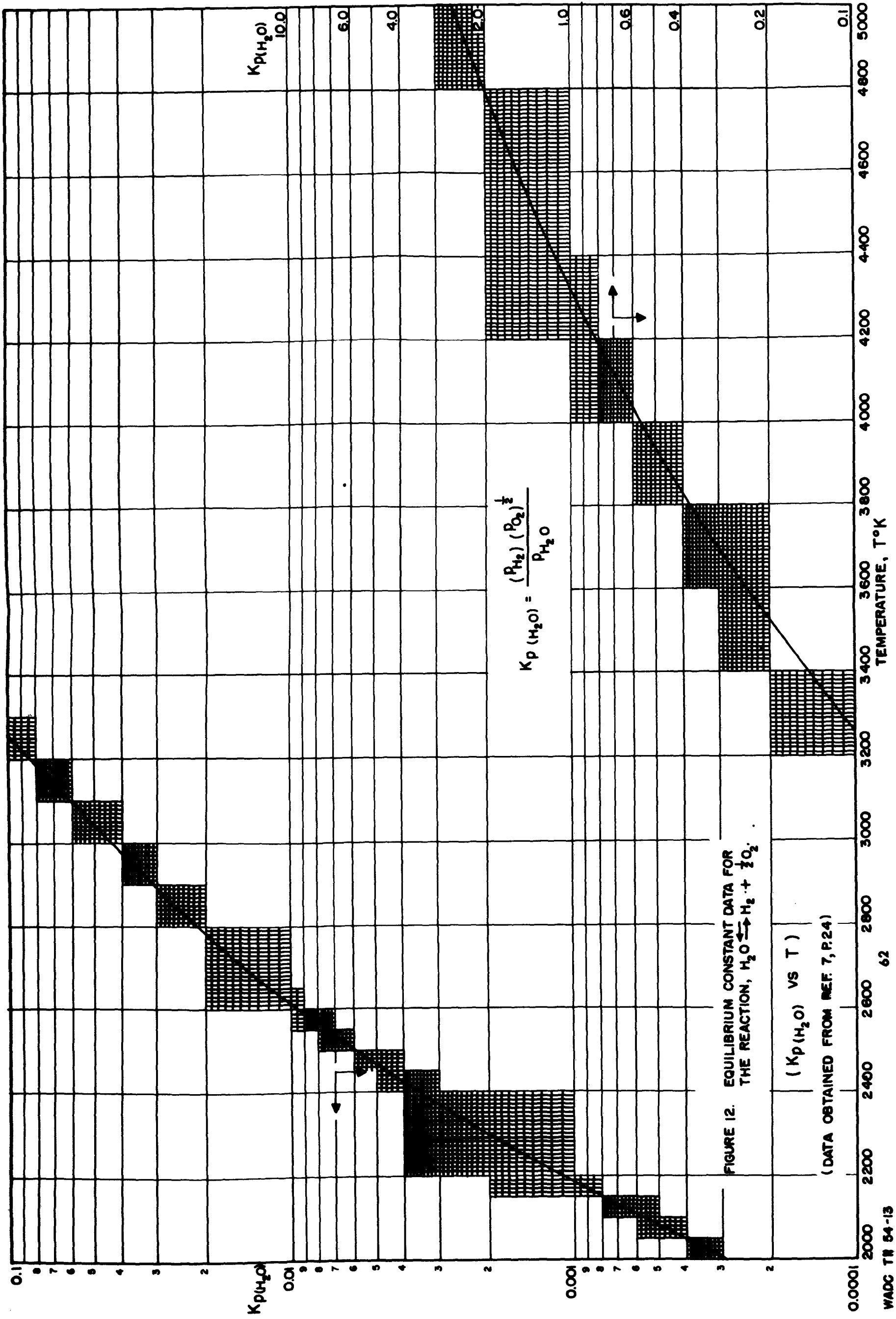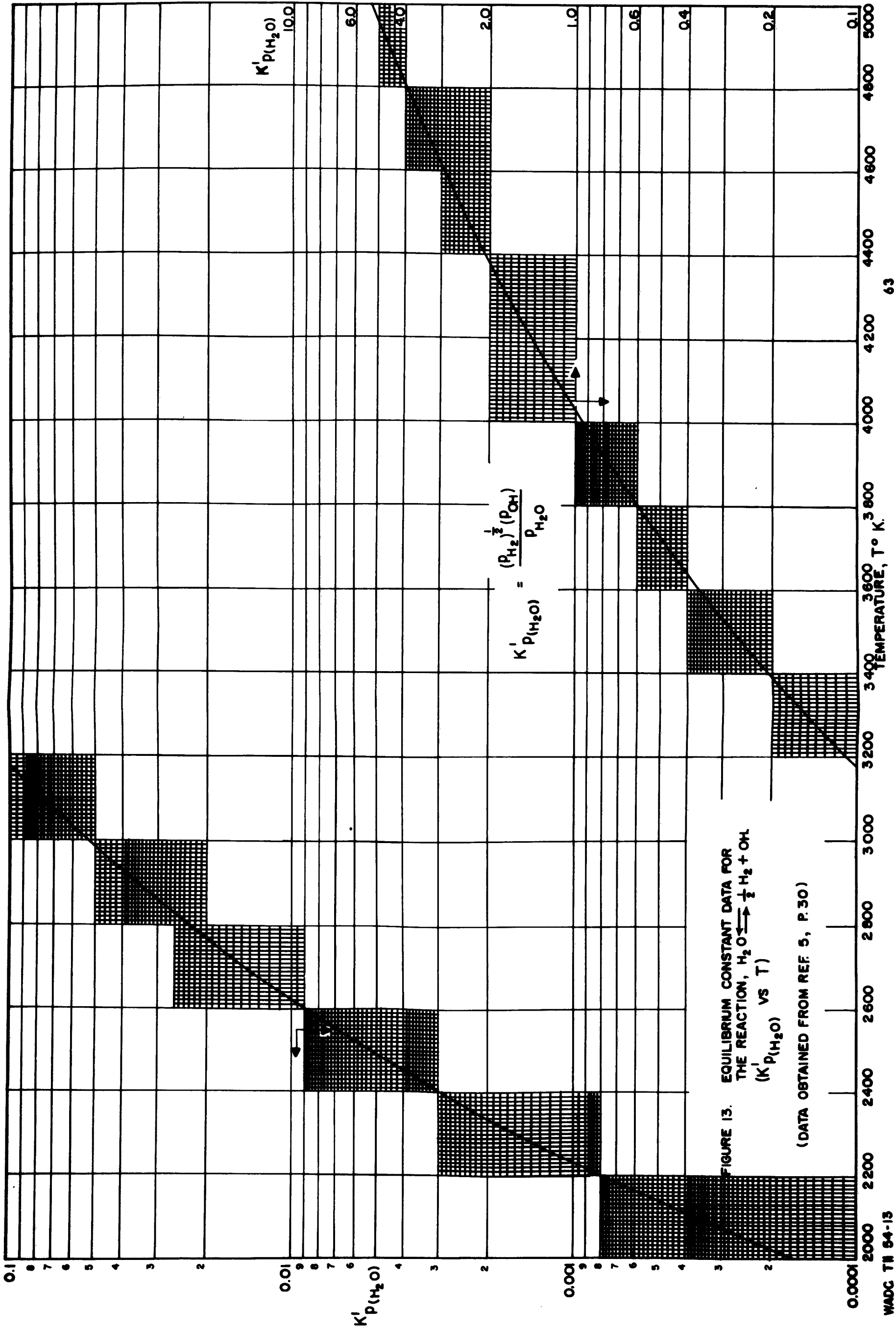
FIGURE 13. EQUILIBRIUM CONSTANT DATA FOR THE REACTION, $H_2O \rightleftarrows \frac{1}{2}H_2 + OH$, ($K'_{P_{(H_2O)}}$ vs T)

$$K'_{P_{(H_2O)}} = \frac{(P_{H_2})^{\frac{1}{2}}(P_{OH})}{P_{H_2O}}$$

(DATA OBTAINED FROM REF. 5, P. 30)

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FIGURE 14. EQUILIBRIUM CONSTANT DATA FOR THE REACTION, $\frac{1}{2}H_2 \rightleftharpoons H$. ($Kp_{(H_2)}$ vs T).

$$Kp_{(H_2)} = \frac{P_H}{(P_{H_2})^{\frac{1}{2}}}$$

(DATA OBTAINED FROM REF 5, P. 30)

TEMPERATURE, $T \,^{\circ}K$.

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$$K_{P(O_2)} = \frac{P_O}{(P_{O_2})^{\frac{1}{2}}}$$

FIGURE 15. EQUILIBRIUM CONSTANT DATA
FOR THE REACTION, $\frac{1}{2}O_2 \rightleftharpoons O$.
$(K_{P(O_2)}$ VS T)

(DATA OBTAINED FROM REF. 7, P 25)
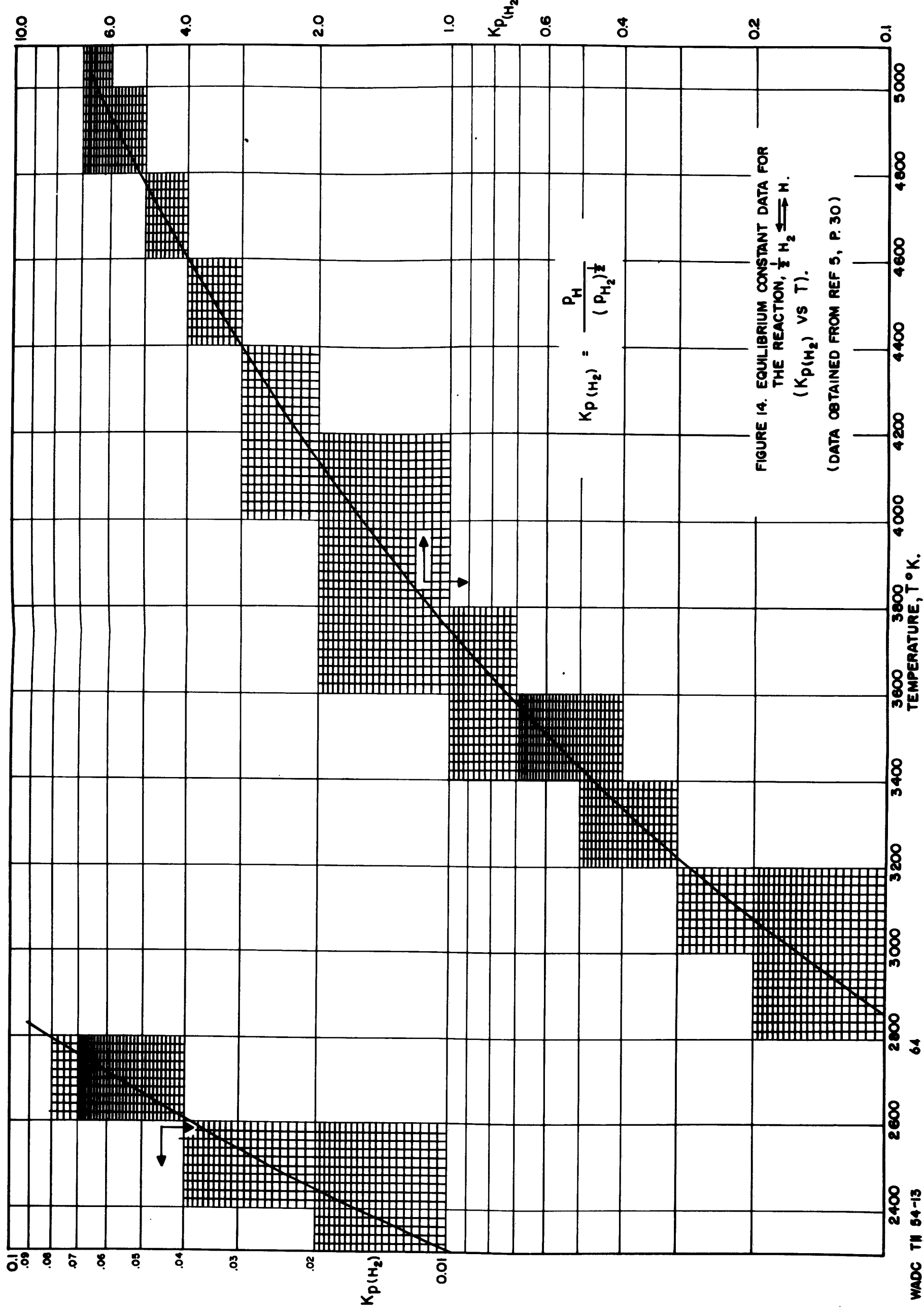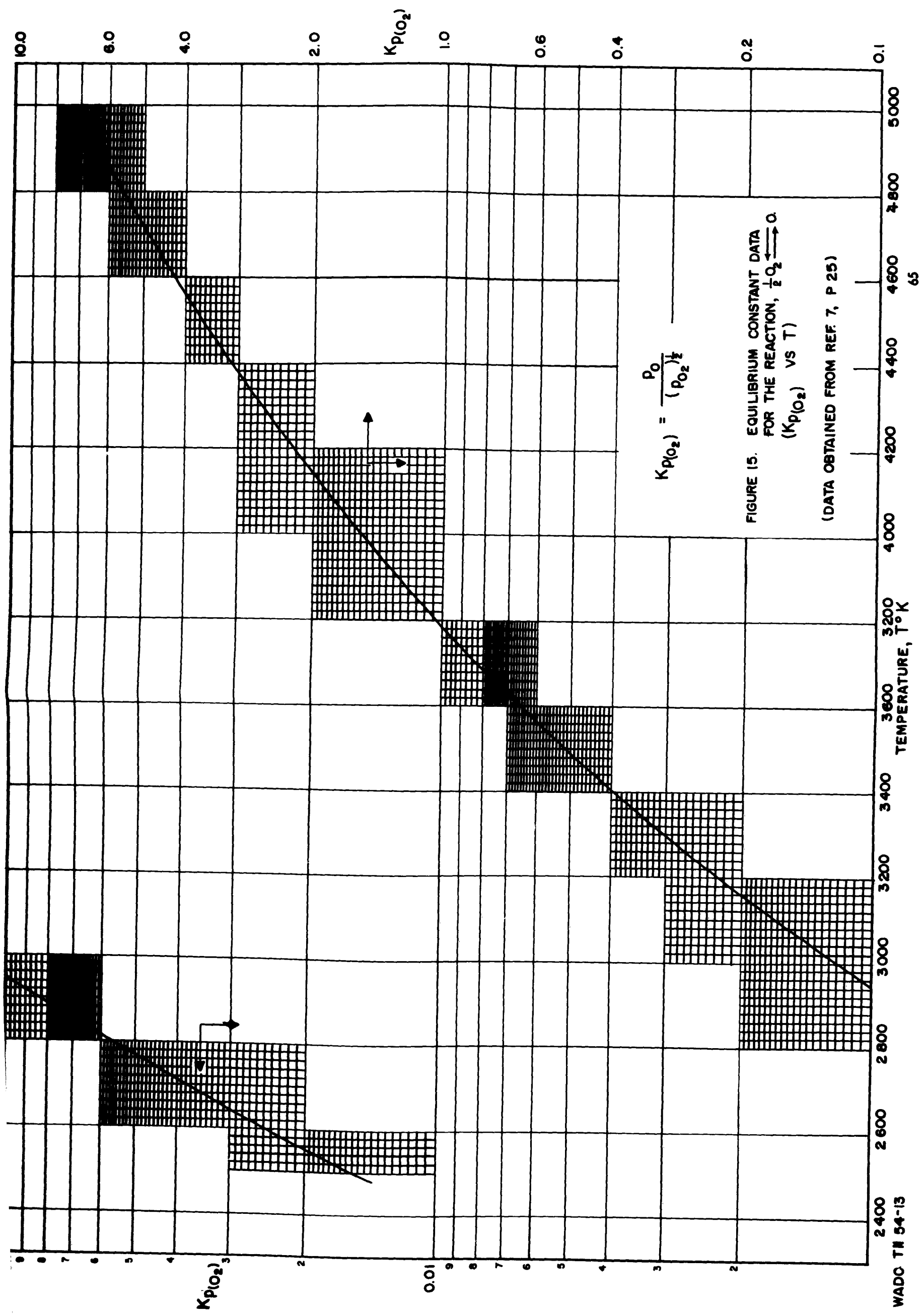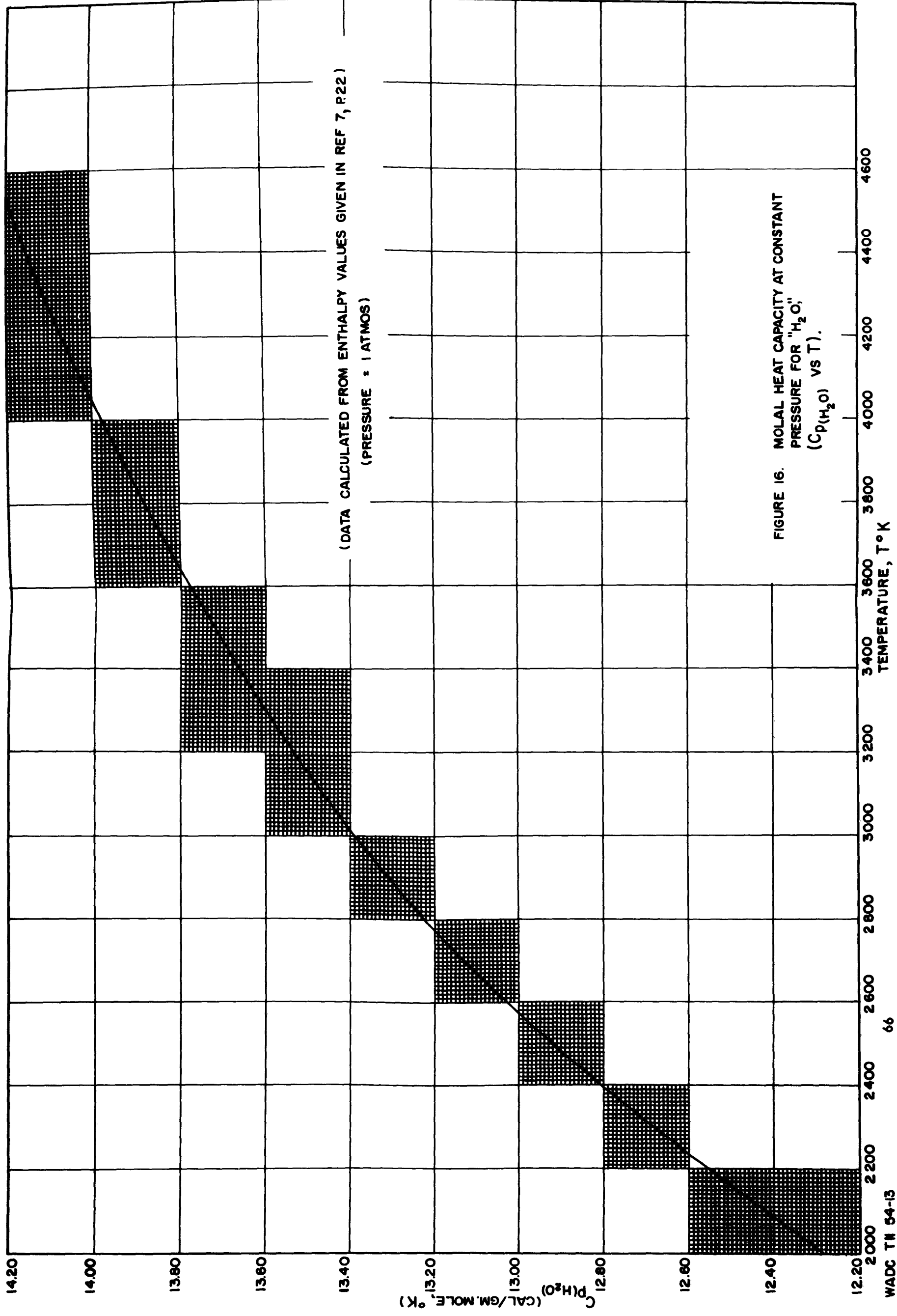
FIGURE 16. MOLAL HEAT CAPACITY AT CONSTANT PRESSURE FOR "H_2O", ($C_{p(H_2O)}$ vs T).

(DATA CALCULATED FROM ENTHALPY VALUES GIVEN IN REF 7, P.22)

(PRESSURE = 1 ATMOS)

TEMPERATURE, T°K

$C_{p(H_2O)}$ (CAL/GM.MOLE, °K)

(DATA CALCULATED FROM ENTHALPY VALUES GIVEN IN REF. 7, P. 22)

(PRESSURE = I ATMOS.)

FIGURE 16. (CONTINUED) MOLAL HEAT CAPACITY AT CONSTANT PRESSURE FOR "H_2O", ($C_{P(H_2O)}$ vs T).

TEMPERATURE, T°K

$C_{P(H_2O)}$ (CAL/GM. MOLE, °K)

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FIGURE 17. MOLAL HEAT CAPACITY AT CONSTANT PRESSURE FOR "H_2"; ($C_{p(H_2)}$ vs T).
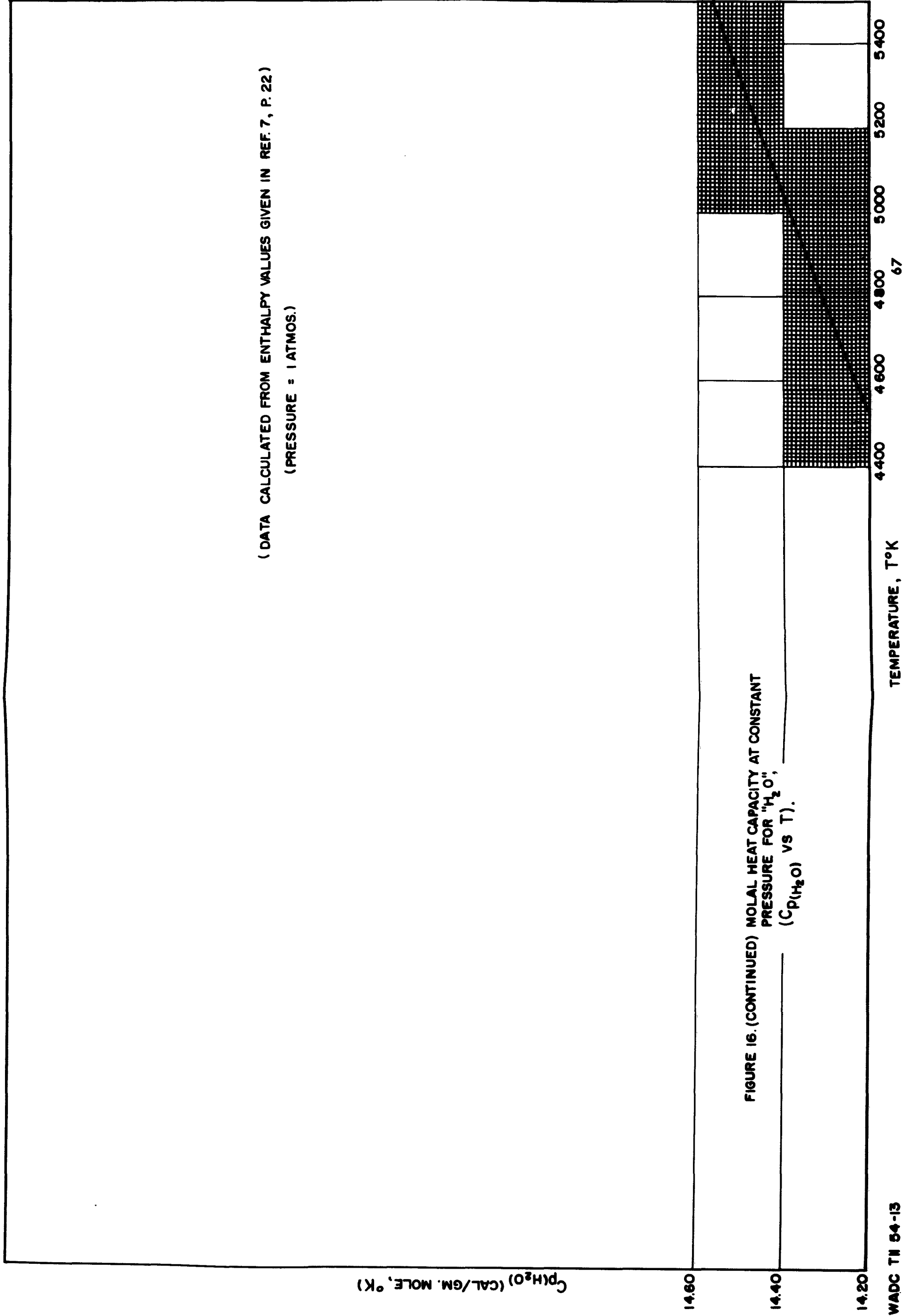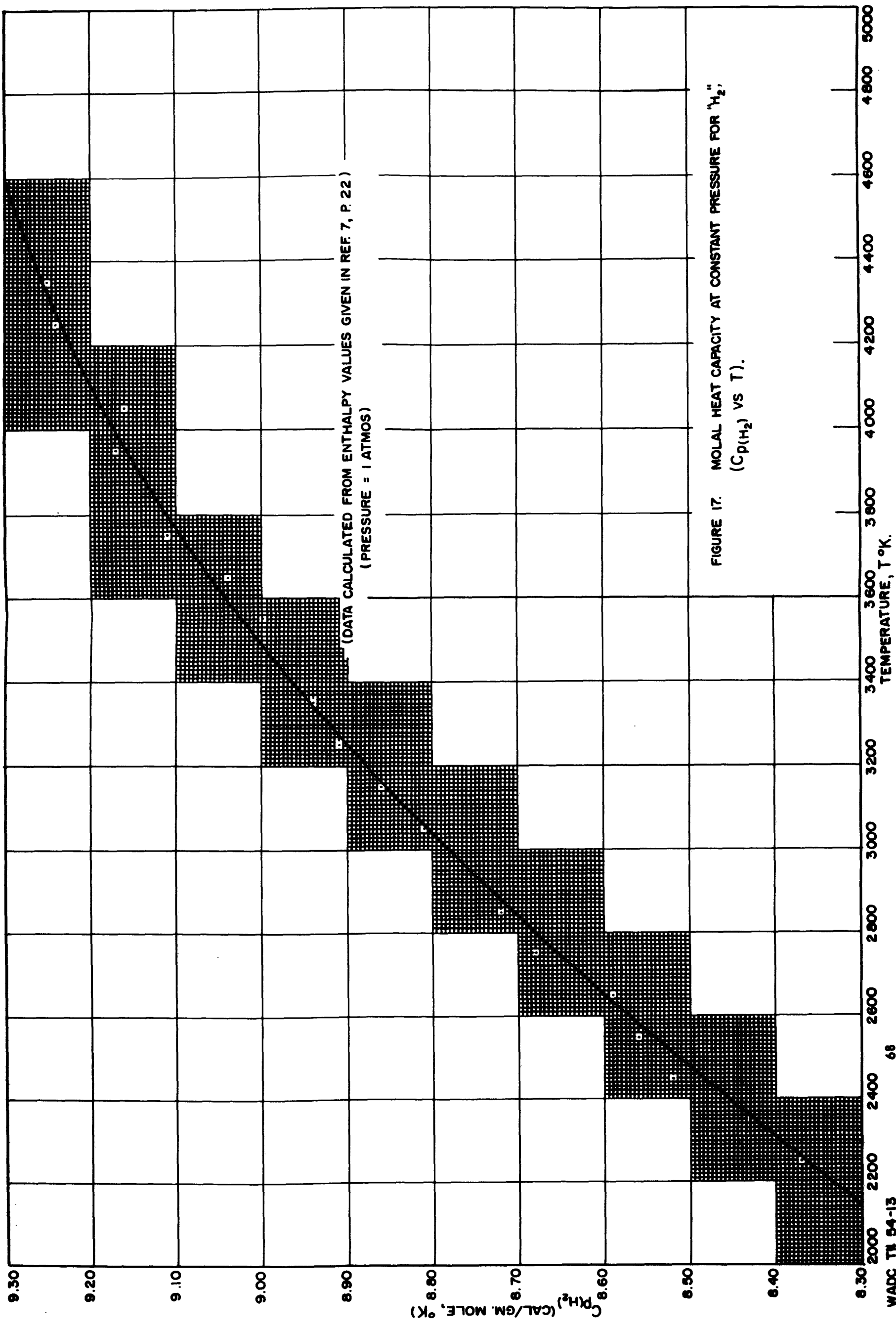
(DATA CALCULATED FROM ENTHALPY VALUES GIVEN IN REF. 7, P. 22) (PRESSURE = 1 ATMOS)
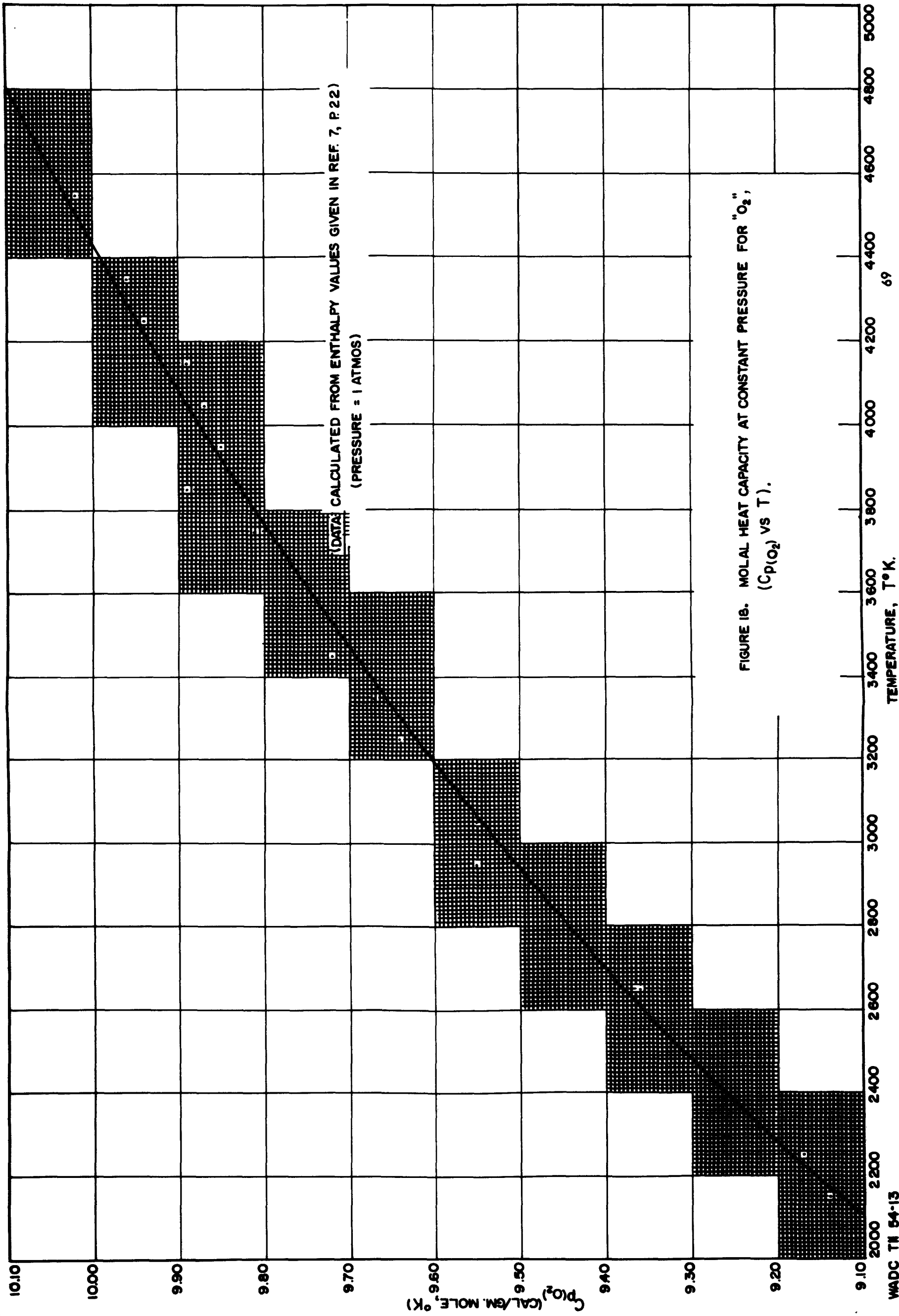
FIGURE 18. MOLAL HEAT CAPACITY AT CONSTANT PRESSURE FOR "O₂," ($C_{p(O_2)}$ vs T).

(DATA CALCULATED FROM ENTHALPY VALUES GIVEN IN REF. 7, P. 22)

(PRESSURE = 1 ATMOS)

TEMPERATURE, T°K.

$C_{p(O_2)}$ (CAL/GM·MOLE, °K)

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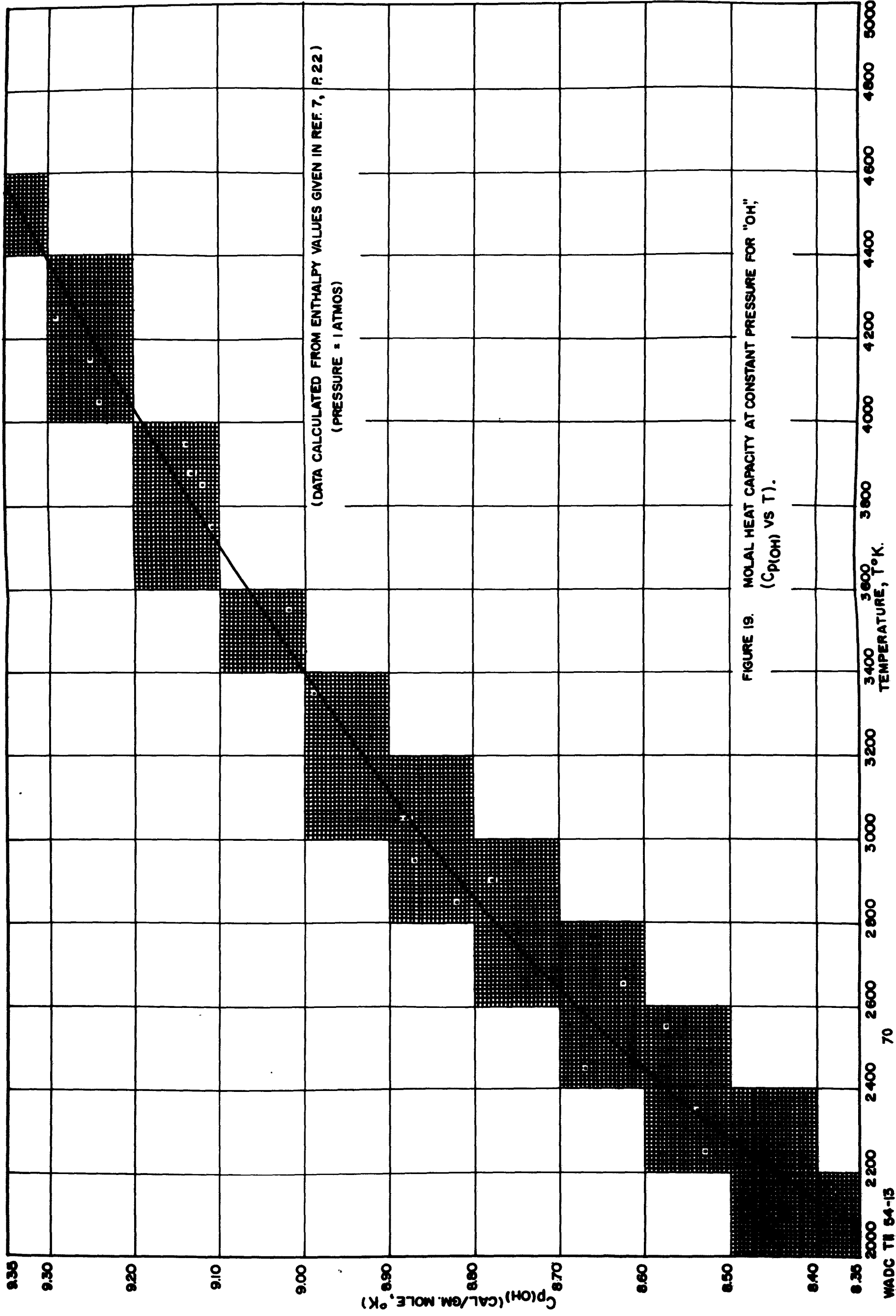
FIGURE 19.   MOLAL HEAT CAPACITY AT CONSTANT PRESSURE FOR "OH",
($C_{p(OH)}$ vs T).

(DATA CALCULATED FROM ENTHALPY VALUES GIVEN IN REF. 7, P. 22)
(PRESSURE = I ATMOS)

TEMPERATURE, T°K.

$C_{p(OH)}$ (CAL/GM. MOLE, °K)

FIGURE 20. DETERMINATION OF COMPOSITION OF FINAL MIXTURE, TRIALS I THROUGH 4, (Δp_{H_2O} VS $p_{H_2(ASSUMED)}$) FOR A $p_{2(ASSUMED)}$ OF 20.00 ATMOS.).

TRIAL NO.	$p_{H_2(ASSUMED)}$	Δp_{H_2O}
I	4.35	+3.6989
2	3.00	-1.8990
3	3.43	-0.3218
4	3.51	-0.0001

$T_{2(ASSUMED)} = 3800\ °K.$

(STOICHIOMETRIC $H_2 - O_2$ MIXTURE)

TRIAL I

TRIAL 4
TRIAL 3
TRIAL 2

Δp_{H_2O}, ATMOS.

$p_{H_2(ASSUMED)}$, ATMOS.

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TRIAL NO.	$p_{H_2(ASSUMED)}$	Δp_{H_2O}
1	4.35	+3.6999
2	3.00	−1.8990
3	3.43	−0.3218
4	3.51	−0.0001
5	3.00	+11.414
6	1.50	−7.7743
7	2.112	+0.47582
8	2.275	+2.3080
9	2.075	+0.07
10	2.070	+0.07
11	2.75	+0.6869
12	2.00	−4.2362
13	2.71	+0.312
14	2.718	+0.369
15	2.652	−0.1039
16	2.64	−0.1894
17	2.663	−0.0257
18	2.670	+0.0288
19	2.60	−1.8052
20	2.62	−1.6947
21	2.70	−1.2317
23	2.91	+0.0401
24	2.90	−0.0215
25	2.70	−1.9767
26	3.00	+0.7869
27	2.92	+0.2612
28	2.90	+0.1382
29	2.881	+0.0158

FIGURE 21. DETERMINATION OF COMPOSITION OF FINAL MIXTURE, TRIALS 1 THROUGH 29, (Δp_{H_2O} vs $p_{H_2(ASSUMED)}$ FOR A $p_{2(ASSUMED)}$ OF 20.00 ATMOS.).

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TRIAL NO.	$T_{2(ASSUMED)}$, °K	$T_{2(CALCULATED)}$, °K
4	3800	2369
10	3300	4476.4
18	3528	3741.3
24	3572	3523.5
29	3560	3589.9

(STOICHOMETRIC $H_2 - O_2$ MIXTURE)

FIGURE 22. DETERMINATION OF FINAL TEMPERATURE, TRIALS I THROUGH 29, ($T_{2(CALCULATED)}$ VS $T_{2(ASSUMED)}$ FOR A $P_{2(ASSUMED)}$ OF 20.00 ATMOS).

TRIAL NO.	$P_{H_2(ASSUMED)}$	ΔP_{H_2O}
30	2.50	- 0.13876
31	2.80	+ 0.87810
32	2.649	+ 0.73050
33	2.537	+ 0.0484
34	2.526	- 0.0170
35	2.50	- 0.76713
36	2.622	- 0.13889
37	2.66	+ 0.08569
38	2.644	- 0.00177
39	2.60	+ 3.82049
40	1.95	- 1.54662
41	2.14	- 0.09542
42	2.15	- 0.06140
43	2.40	- 0.26472
44	2.44	- 0.01181

(STOICHIOMETRIC $H_2 - O_2$ MIXTURE)

TRIALS 43 THRU 44
$T_{2(ASSUMED)} = 3528\ °K$

TRIALS 30 THRU 34
$T_{2(ASSUMED)} = 3560\ °K$

TRIALS 35 THRU 38
$T_{2(ASSUMED)} = 3605\ °K$

TRIALS 39 THRU 42
$T_{2(ASSUMED)} = 3420\ °K$

FIGURE 23. DETERMINATION OF COMPOSITION OF FINAL
MIXTURE, TRIALS 30 THRU 44,
(ΔP_{H_2O} VS $P_{H_2(ASSUMED)}$ FOR A
$P_{2(ASSUMED)}$ OF 17.00 ATMOS).

$P_{H_2(ASSUMED)}$, ATMOS.

ΔP_{H_2O}, ATMOS.

TRIAL NO.	T_2(ASSUMED),°K	T_2(CALCULATED),°K
34	3560	3442.6
38	3605	3233.4
42	3420	3998.5
44	3528	3572.5

(STOICHIOMETRIC $H_2 - O_2$ MIXTURE)

CORRECT VALUE OF T_2 CORRESPONDING TO A P_2(ASSUMED) OF 17.00 ATMOS. = 3536 °K
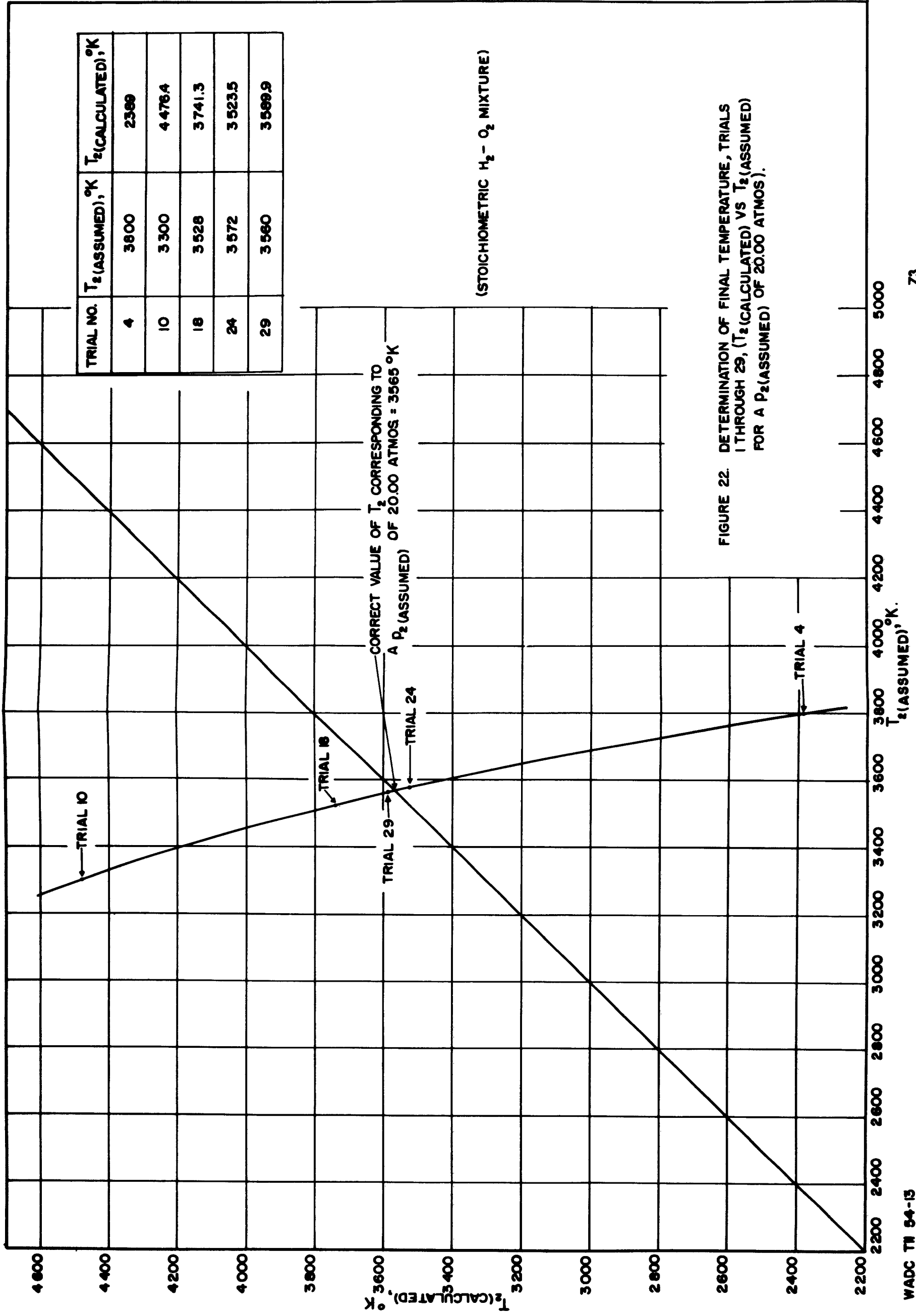
←TRIAL 42

←TRIAL 34

←TRIAL 44

←TRIAL 38

FIGURE 24. DETERMINATION OF FINAL TEMPERATURE, TRIALS 30 THROUGH 44, (T_2(CALCULATED) VS T_2(ASSUMED) FOR A P_2(ASSUMED) OF 17.00 ATMOS).

T_2(ASSUMED), °K

T_2(CALCULATED), °K

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TRIAL NO.	$p_{H_2(ASSUMED)}$	Δp_{H_2O}
45	2.40	-0.532644
46	2.472	-0.08884
47	2.477	-0.05723
48	2.467	-0.12081
49	2.486	-0.00054

(STOICHIOMETRIC $H_2 - O_2$ MIXTURE)

$T_{2(ASSUMED)} = 3536\ ^\circ K.$

$(\Delta p_{H_2O}$ VS $p_{H_2(ASSUMED)}$ FOR A $P_{2(ASSUMED)}$ OF 17.17 ATMOS.)

$p_{H_2(ASSUMED)}$, ATMOS.

Δp_{H_2O}, ATMOS.
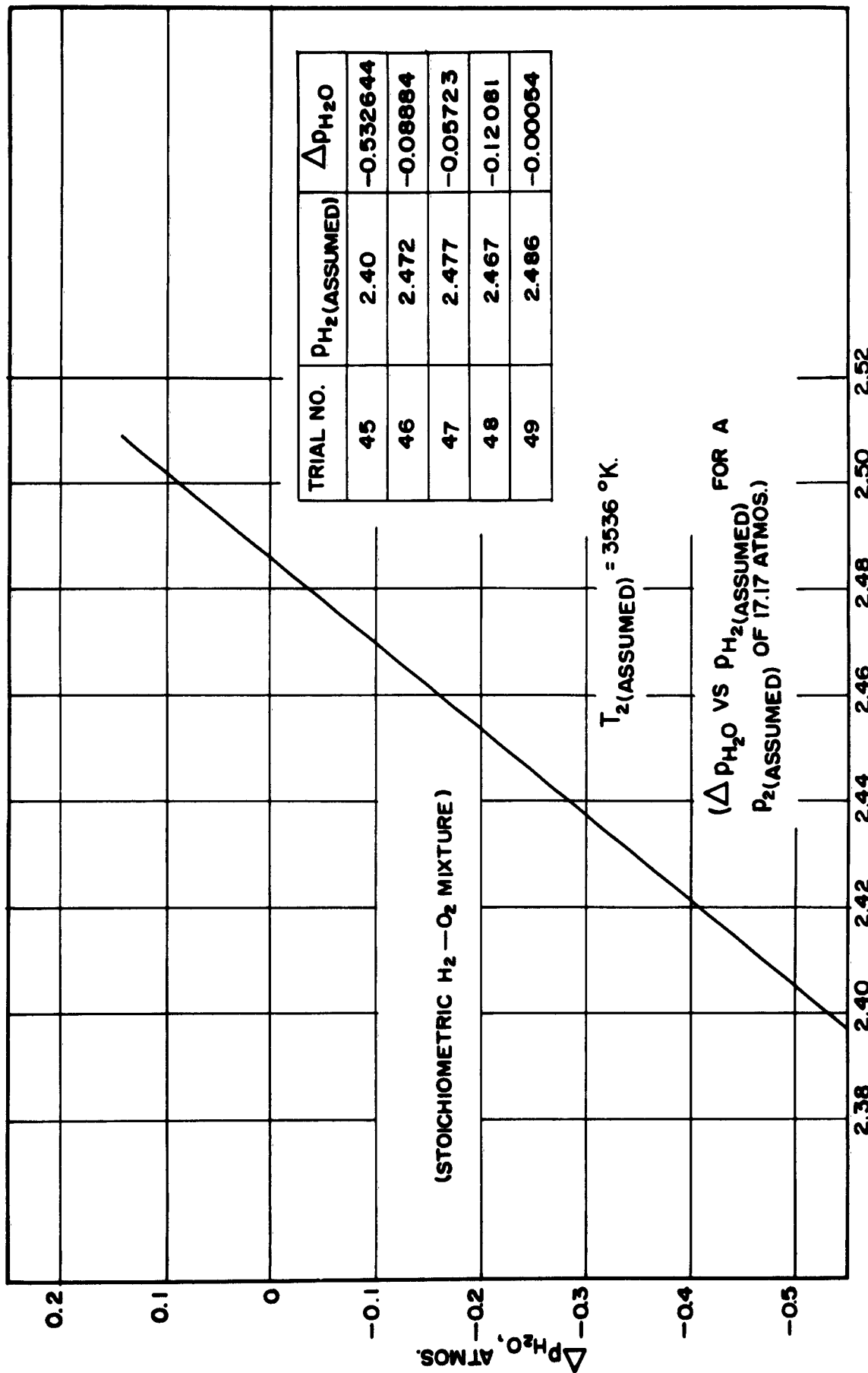
FIGURE 25. DETERMINATION OF COMPOSITION OF FINAL MIXTURE, TRIALS 45 THROUGH 49.
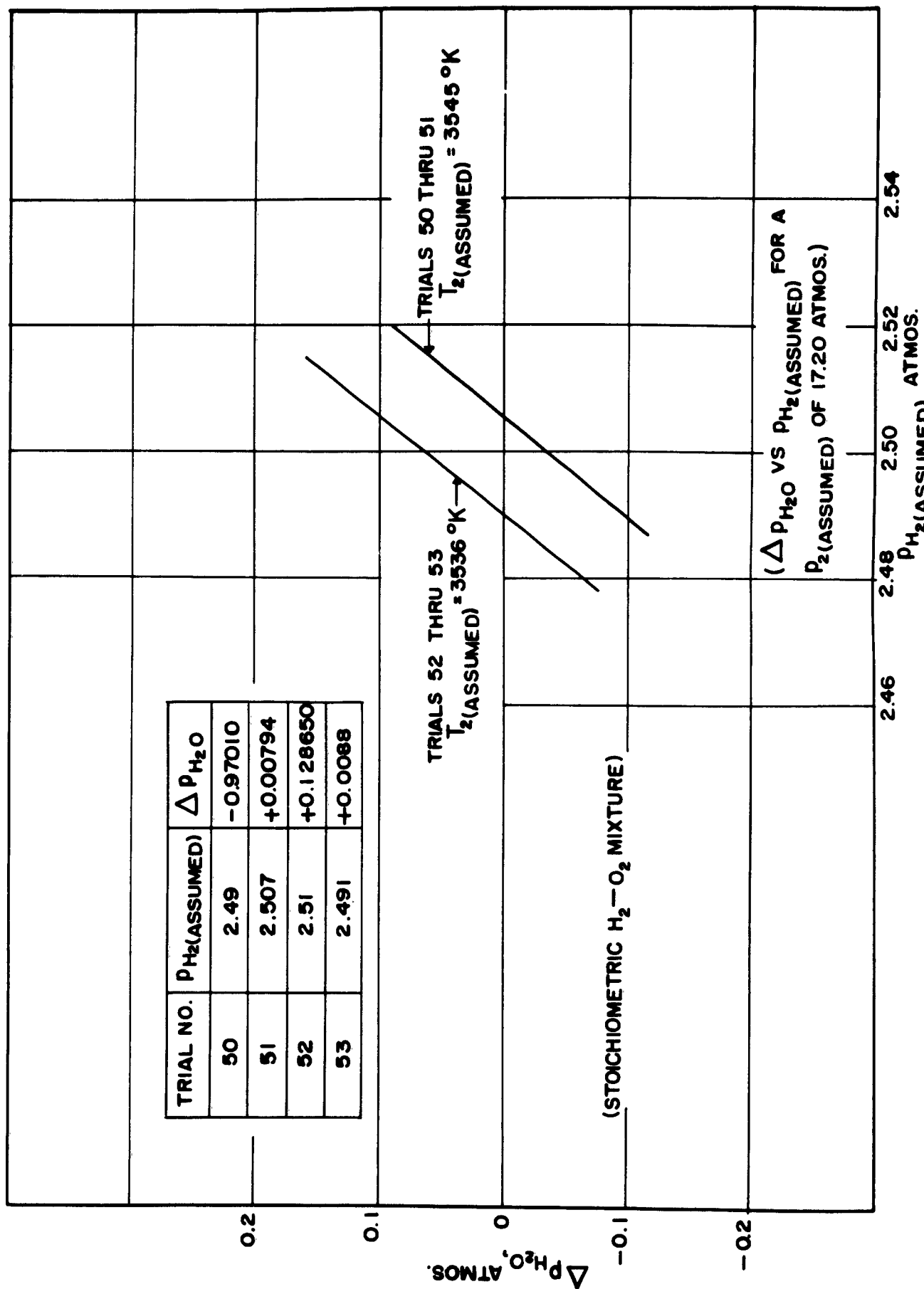
FIGURE 26. DETERMINATION OF COMPOSITION OF FINAL MIXTURE, TRIALS 50 THROUGH 53.

TRIAL NO.	$T_{2(\text{ASSUMED})}$	$T_{2(\text{CALCULATED})}$
51	3545	3513.6
53	3536	3546.8

CORRECT VALUE OF T_2 CORRESPONDING TO A $p_{2(\text{ASSUMED})}$ OF 17.20 ATMOS = 3538 °K.

FIGURE 27. DETERMINATION OF FINAL TEMPERATURE, TRIALS 50 THROUGH 53 ($T_{2(\text{CALCULATED})}$ VS $T_{2(\text{ASSUMED})}$ FOR A $p_{2(\text{ASSUMED})}$ OF 17.20 ATMOS.

TRIAL NO.	$P_{2(ASSUMED)}$ ATMOS.	$P_{2(CALCULATED)}$ ATMOS.
29	20.00	17.3887
44	17.00	17.3257
49	17.17	17.2203
53	17.20	17.2269

(STOICHIOMETRIC $H_2 - O_2$ MIXTURE)

$P_{2(ADJ.)} = 17.22$ ATMOS.

TRIAL 53

TRIAL 44.

TRIAL 49

TRIAL 29

FIGURE 28. DETERMINATION OF FINAL PRESSURE, $(P_{2(CALCULATED)}$ VS $P_{2(ASSUMED)})$.

$P_{2(ASSUMED)}$, ATMOS.

$P_{2(CALCULATED)}$, ATMOS.